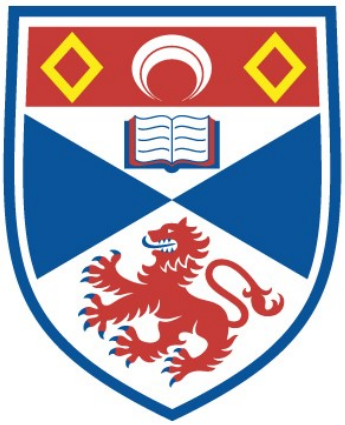
STUDIES OF QUENCHING OF EXCITED STATES OF AROMATIC MOLECULES IN POLYMER MATRICES

Alwan Nsayiff Jassim

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1980

STUDIES OF QUENCHING OF EXCITED STATES OF AROMATIC MOLECULES IN POLYMER MATRICES

A Thesis

presented for the degree of

DOCTOR OF PHILOSOPHY

in the Faculty of Science of the

University of St. Andrews

by

ALWAN NSAYIFF JASSIM, B.Sc.

April 1980

United College of St. Salvator
and St. Leonard, St. Andrews.

TO MY WIFE

Certificate

I hereby certify that Alwan N. Jassim has spent 9 terms of research under my supervision has fulfilled the Conditions of Ordinance No. 12 (St. Andrews) and is qualified to submit this thesis in application for the degree of Doctor of Philosophy.

J.R. MacCallum
Director of Research

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

This thesis describes results of research carried out at the Chemistry Department, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Dr. J.R. MacCallum since the 1st of January, 1978.

A.N. JASSIM

ACKNOWLEDGEMENTS

I should like to record my gratitude and thanks to Dr. James R MacCallum for his help and encouragement in all aspects of this work

My thanks are also due to Dr. T.M.. Shepherd for his help, to Mr James Rennie and Mr. J.G. Ward for their technical aid.

Finally, I am indebted to the IRAQI GOVERNMENT for the financial support during my work.

A.N. JASSIM

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Summary

The phosphorescence behaviour of a series of polycyclic aromatic compounds has been studied in different polymer matrices. Measurements have been carried out at 77K and from room temperature up to 350K. Studies at 77K have shown that the polymer matrix takes part in some quenching reaction, the rate constant depending on the additive being studied. At higher temperatures non-exponential decays were observed, for polystyrene this phenomenon is very marked. It is proposed that the cause of non-exponential decay is T-T annihilation resulting from mobile triplet exciton migration within the polymer matrix. It is proposed that the triplet levels are 285.9 and 297.4 kJ $mole^{-1}$ for polystyrene and poly(methylmethacrylate) respectively.

The quenching of fluorescence for the polycyclic aromatic additives by oxygen has been examined and unusual plots obtained. At low pressures of oxygen enhanced singlet emission was observed but as the pressure was increased normal Stern-Volmer plots were obtained. Simultaneously as pressure of O_2 increased the triplet emission was very efficiently quenched and the increase in fluorescence was observed. When the phosphorescence ceased the intensity of singlet emission decreased with increasing pressure of O_2. The mechanism proposed to account for this very unusual behaviour involves paramagnetic quenching of the singlet state by the mobile triplet exciton. The increase in fluorescence resulting from removal of the triplet exciton by oxygen is greater than the direct singlet quenching by O_2.

CHAPTER 1

INTRODUCTION

Photophysical processes

Before introducing detailed discussion of this work a few elementary facts about the photochemistry of aromatic molecules and different plastics need to be known.

Most polyatomic organic molecules are chemically stable and contain an even number of electrons which are paired; thus their ground states are singlet. Photoexcitation raises one electron to a higher quantum state in which it is spin can remain antiparallel to its "partner", so that the multiplicity is still singlet. Alternatively it may become parallel to its partner, so that the multiplicity is three and a set of triplet energy is formed[1]. A triplet state has a lower energy than the corresponding singlet state[2,3].

The excess energy of a molecule in its excited state may be dissipated by the following processes[4]:

- Radiative processes: fluorescence and phosphorescence.
- Radiationless processes.
- Bimolecular deactivation processes.
- Dissociation processes.

Those processes can be depicted by means of an energy-level diagram, called a Jablonsky[5] diagram (fig. 1.1).

(I) Radiative processes

(1) Fluorescence

Fluorescence can be described as radiation emitted in a

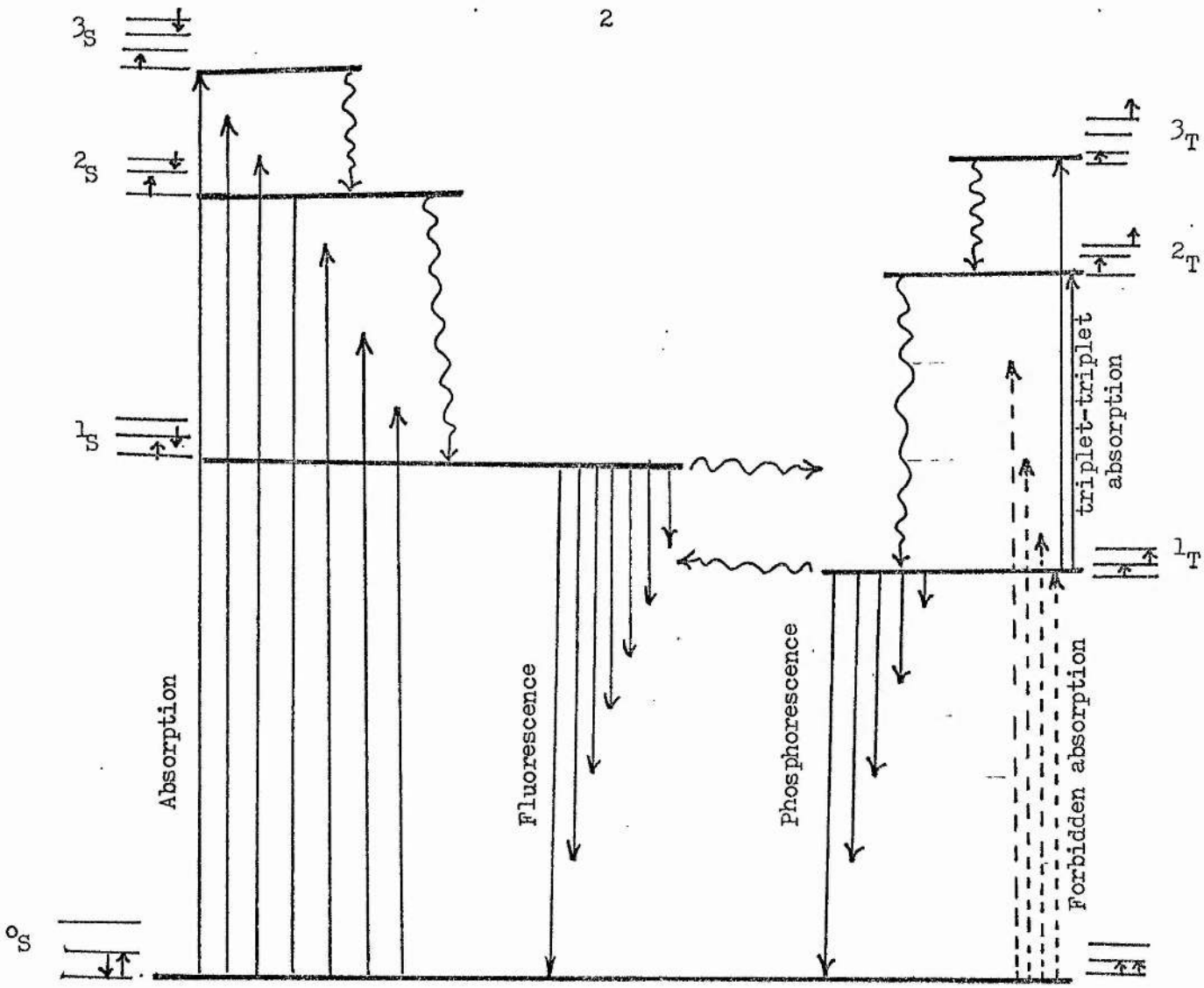


Figure 1.1

Modified Jablonsky diagram for the most important processes involving electronically excited states. Broken lines for the forbidden processes, the solid for the spin allowed and the wavy for the internal and intersystem processes.

transition between the two lowest singlet states:

$$^1S \longrightarrow {}^0S + h\nu \qquad 1.1$$

Also it has been reported from triplet-triplet transition in fluid and rigid solution[6-12]:

$$^2T \longrightarrow {}^1T + h\nu \qquad 1.2$$

so that the fluorescence can be defined in general way as emission produced in transition between states of the same multiplicity[13]. Fluorescence is rapid with the rate constant for the process, k_f, about 10^6 - 10^9 s^{-1}.

Fluorescence intensity can be recorded as a function of time, quencher concentration or of any other variable such as temperature. Varying fluorescence intensity with temperature is unexpected. It seems[14-16] that the process is intersystem crossing (ISC) from ^1S to a higher triplet ^nT which is isoenergetic with ^1S. The effect of temperature is to increase the population of higher vibrational and rotational sub-levels of ^1S from which faster intersystem crossing may occur, (Fig. 1.1) and Q_f drops accordingly[2,27].

(2) Phosphorescence

Phosphorescence is the result of transition between states of different multiplicity, typically ^1T-^0S. The process being spin forbidden, has a much smaller rate constant ($k_p \sim 10^{-2}$ - 10^4 S^{-1}) than that for fluorescence[17]. Since the pioneering work of Lewis and co-workers with fluorescein in boric acid glass[18],

phosphorescence has been observed from many other species in rigid media. It has also been observed in deoxygenated solutions at room temperature[19-26], and even at a temperature as high as 70°C[27].

(II) Radiationless processes

A radiationless process converts one electronic state to another without the emission of light[4]. It can occur as a result of:

(1) Internal conversion

This process occurs between two different electronic states of the same multiplicity, i.e. singlet-singlet ($^2S \rightsquigarrow {}^1S$, $^1S \rightsquigarrow {}^0S$) or triplet-triplet process ($^2T \rightsquigarrow {}^1T$), as presented in Fig. 1.1

(2) Intersystem crossing

Intersystem crossing is a process occurring between singlet and triplet states ($^1S \rightsquigarrow {}^1T$), or ($^1T \rightsquigarrow {}^0S$) accompanied with spin inversion, as shown in Figure 1.1. The important radiative and nonradiative steps are listed in Table 1.1

Table 1.1

Important processes involving electronically excited states

Step	Reaction	Rate
Excitation	$^0S + h\nu \longrightarrow {}^1S$	I_a
Fluorescence	$^1S \longrightarrow {}^0S + h\nu'$	$k_f [{}^1S]$
Internal conversion	$^1S \longrightarrow {}^0S$ + heat	$k_{IC} [{}^1S]$
Intersystem crossing	$^1S \longrightarrow {}^1T$ + heat	$k_{(ISC)_S} [{}^1S]$
Phosphorescence	$^1T \longrightarrow {}^0S + h\nu''$	$k_p [{}^1T]$
Intersystem crossing	$^1T \longrightarrow {}^0S$ + heat	$k_{(ISC)_T} [{}^1T]$

(III) Energy transfer and migration

The term energy transfer means the transfer of the electronic excitation energy of a chromophore to another chromophore of a different species. Similar transfer to an aromatic chromophore of the same species is described as energy migration[71]. In the light of our results, we shall focus on energy transfer and migration in polymers glasses.

Energy transfer in polymers

Studies in energy transfer in polymer are very important as this transfer is directly related to the effects of stabilization and photodegradation[45,46]. In polymers, energy transfer can occur by inter- or intra-molecular energy transfer.

(1) Intermolecular energy transfer

This process occurs between an excited polymer chromophore (donor) and the (acceptor) molecule, or between an excited aromatic chromophore (donor) and polymer molecule (acceptor) under different conditions[4]:

(i) - when the two molecules come into molecular contact, i.e. their centres are separated by the sum of their molecular radii;

(ii) - when the two molecules are separated by distances larger than the sum of their molecular radii, and the quenching by energy transfer is not influenced by diffusion. The energy transfer between a polymer (donor, D) and an acceptor (A) molecule may occur:

a - From the excited singlet state of the donor:

$$^1D + {}^oA \longrightarrow {}^oD + {}^1A \qquad 1.3$$

b - From the triplet excited state of the donor:

$$^3D + {}^oA \longrightarrow {}^oD + {}^1A \qquad 1.4$$

$$^3D + {}^oA \longrightarrow {}^oD + {}^3A \qquad 1.5$$

The energy level of the excited donor state has to be higher than that of the acceptor. Typical triplet-triplet energy transfer in polymers was found by Geuskens[47], to occur between solid poly(vinyl benzophenone) and naphthalene. This is illustrated in figure 1.2. Cozzens and Fox[51] claimed in 1968 that naphthalene is the acceptor in naphthalene/polymethylmethacrylate system for both singlet and triplet energy transfer, although the work has never been fully published. Others used perdeuteronaphthalene ($C_{10}D_{10}$) in polystyrene matrix to prove singlet[52] and triplet[53] energy transfer. The critical distances for energy transfer in polymer system are shown in Table 1.2.

Table 1.2

The critical distance R_o(nm) for energy transfer between donor and acceptor molecules

Donor	Acceptor	Type of energy transfer	R_o (nm)	Reference
Poly(methylvinylketone)	Naphthalene	T-T	2.6	54
Poly(methylvinylketone)	Naphthalene	T-T	1.1	55
Poly(vinylnaphthalene)	Piperylene	T-T	1.5	56
Polystyrene	1,1,4,4-Tetra-phenylbutadiene	S-S	2.1	57
Polyacynaphthalene	Benzophenone	S-S	1.5	56

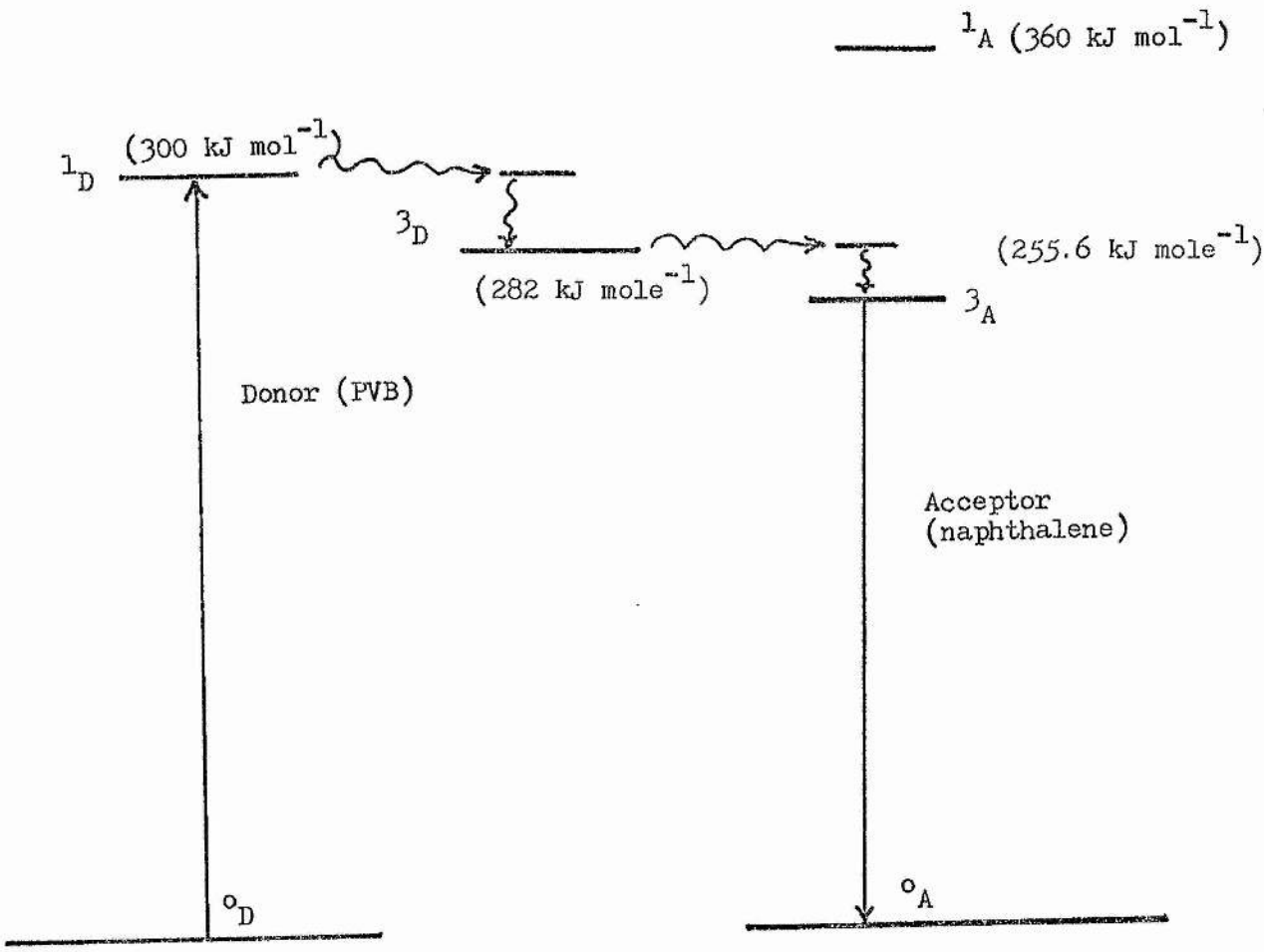


Figure 1.2

Diagram of energy level for the system (PVB/N).

The probability of energy transfer increases with increasing life time of the excited state. Long-lived excited triplet states are more likely to participate in energy transfer than short-lived excited singlet state of the same molecule. The triplet-triplet energy transfer is only allowed by the exchange mechanism of transfer of energy (i.e. the electron clouds of the acceptor and of the donor overlap, and transfer due to short range interaction, 1-1.5 nm), and forbidden for the resonance-excitation transfer[71]. In resonance excitation transfer, the reaction can take place efficiently over distances greater than molecular diameters (i.e. 5-10 nm).

(2) Detection of energy transfer

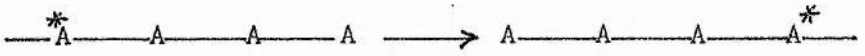
It is worthwhile mentioning that the triplet-singlet energy transfer: $^3D + {}^oA \longrightarrow {}^oD + {}^1A$ can be detected in the form of a reduced life-time of donor phosphorescence, occurring in the presence of an acceptor[1,4]. Moreover, in order to establish that triplet-triplet energy transfer is effected by a resonance mechanism, it is necessary to determine either the life-time[47], or the efficiency of the donor triplet emission in relation to the concentration of the acceptor[48].

Guillet and his co-workers have found that the fluorescence of a low molecular weight compound e.g. naphthalene can be quenched by ethylene-carbon monoxide copolymer[49] in fluid and rigid solutions, and by poly(vinylketone) in solution[50].

(3) Energy migration

The interaction of a singlet-excited molecule ^1S with its neighbours leads to a rapid multi-step transfer of the electronic excitation over a large distance through the crystal[58,59], rigid media or through the solvent[60]. This section is concerned with

energy migration in solid solutions of polymers. Different parts of the same macromolecule can at the same time absorb two or more photons, forming excited singlet states, which may change over by intersystem crossing to the triplet manifold. In crystalline parts of a polymer, having a high degree of symmetry, it is assumed that the excitation energy is not localized in one group but it can be shifted along the chain:



The life-time of migration exciton is about 10^{-8}s. During that time it may "VISIT" several molecules over a long distance (10-10^5 nm). Such a delocalised migrating exciton may be captured by impurities or traps and lose its energy. The exciton may be triplet or singlet.

Now, when two or more migrating triplet exciton are in the same macromolecule, "mutual annihilation", may occur and for example delayed fluorescence is observed. This mechanism may be important for deactivation of an excited polymer molecule[61].

(4) Intramolecular energy transfer in polymers

Intramolecular energy transfer may occur within macromolecules and can in principle be considered as an energy transfer between different parts or segments of the same molecule. One process of polymer intramolecular transfer may occur between closely situated conjugated chromophores, by forming dissociating excimers.

(5) Excimers

In concentrated solution or in solid state, some organic compounds when electronically excited may associate with a molecule in its ground state and form a short lived excited dimer called "excimer" ($^*D$)[62-66]

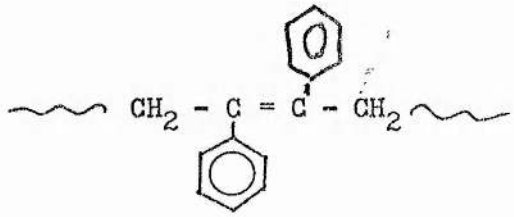
$$^*A + {}^oA \longrightarrow {}^*D$$

Formation of an excimer is accompanied by the appearance of a new emission at longer wavelengths[17]. The emission spectrum is without structure, and the quantum yield is temperature dependent[67-69]. Since Förster and Kasper discovered and interpreted excimer emission from pyrene in solution[70], the phenomenon has been observed in crystalline and emorphous materials[71,74]. It is found that the interaction of an excited molecule with one in the ground state is much stronger than the interaction between two ground state species[73]. Excimer of polystyrene will be considered in detail in the following section.

(IV) Polystyrene (Pst) Luminescence

(1) Fluorescence

In all forms of polystyrene in solution both monomer and excimer emission is observed[74-79]. In the solid the formation of both intra- and inter-chain excimer formation is possible, and monomer (single chromophore) and excimer emission are observed[76,80-84]. Polystyrene film 20-30 μ thick was studied at room temperature and 77 K[85]. At room temperature, only excimer emission with λ_{max} at 324 nm was observed. At 77 K the emission consisted of excimer fluorescence with λ_{max} at 324 nm and another emission at shorter wavelength (285 nm), due to normal fluorescence. Commercial and laboratory prepared Pst also exhibits an 'anomalous' fluorescence with emission maxima at 338, 335, 372 and 385[85] nm. This emission has been attributed to presence of trans-stilbene linkages[86]:



(2) Phosphorescence

Commercial and even laboratory Pst samples which have been carefully prepared and purified, showed phosphorescence at (400-550)nm at room temperature. This emission has been assigned to the prescence of acetophenone-type terminal groups[84,87,88]. Careful purification of Pst has no influence on the phosphorescence spectra, which indicates that the (C=O) group is attached to the polymer[84]. Decay time for Pst phosphorescence at 77 K was found to be 3 sec. Moreover, the phosphorescence of the phenyl group which should be observed in the region of 345 nm has never been detected[90].

Finally, the various fates of the excitation energy in Pst are represented diagrammatically in figure 1.3[73].

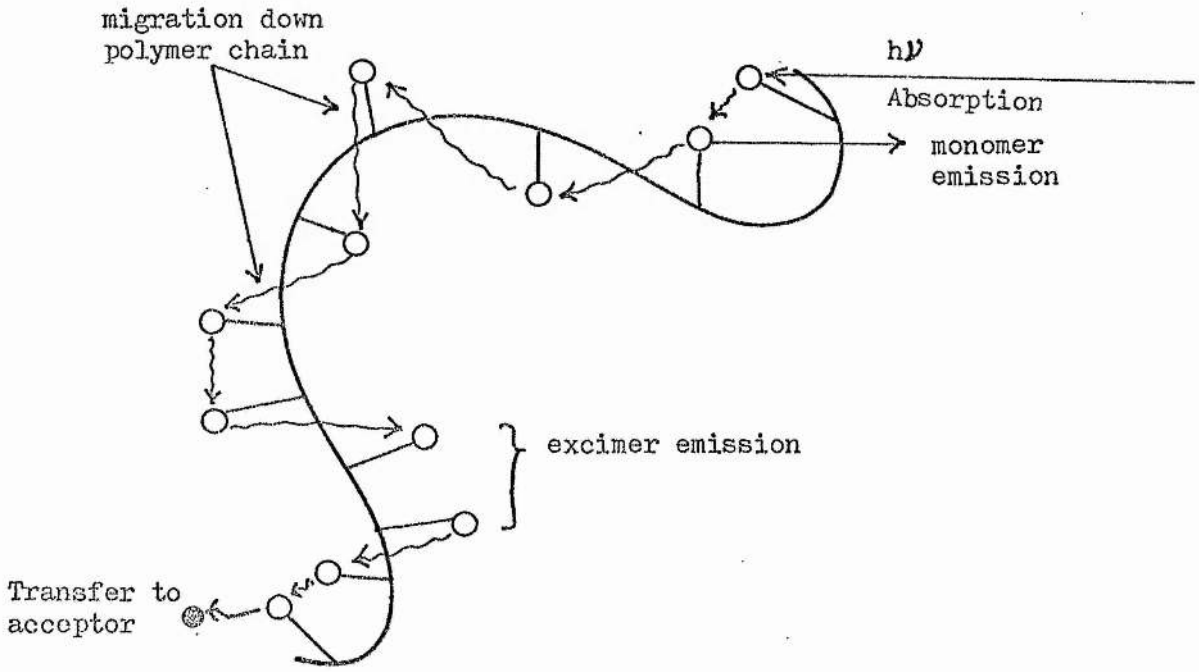


Figure 1.3

(V) Phosphorescence and temperature

After excitation of the lowest singlet state the molecule emits normal fluorescence, returning to a highly vibrationally excited ground state by internal conversion (IC), or undergoes an intersystem crossing (ISC) to ^1T (Fig. 1.1).

A molecule in the lowest triplet state has a relatively long life-time since it is effectively "trapped" there until it:

a - emits the "forbidden" radiation, phosphorescence,

b - acquires thermal energy equal to ΔE_{ST}, which is improbable at low temperatures, to go back to the ^1S state and emit the delayed fluorescence, or

c - undergoes another intersystem crossing to a highly vibrationally excited ground state ^vS, which rapidly goes to the ground state ^oS.

Thus, at low temperature, in rigid media and in the absence of quencher, phosphorescence can compete with processes b and c.

Experimental attempts to measure the temperature dependence of the first order decay of triplet states of molecules are complicated by impurity quenching, especially by O_2. Indeed thorough outgassing of the solution leads to increased life-time of the excited triplet states, but it is not possible to observe the same life-time as in a glass at 77 K. How much is a true temperature or phase effect, and how much is due to the prescence of quencher is not clear[32].

Dissolving aromatic molecules in clear plastic matrices (e.g. PMMA or Pst) would prevent significant molecular diffusion, even at room temperature, then it should be possible to assess the

intrinsic temperature dependence. Experiments of this nature have already been made by many workers[28-31,33-36,72].

Although the natural life-time of phosphorescence (phos.) is independent of temperature, the observed rate of decay of the triplet state is the sum of competing processes, phos., ISC back to ^1S or to ^vS_o, and bimolecular reactions with other substances. If one of these processes is varying with temperature, the phos. life-time will appear to be temperature dependent[1].

Some of the important literature explanations may be summarized as follows:

i) The temperature dependence of phos. characteristics is associated with an intermolecular non-radiative decay event[33].

ii) The temperature dependence of phos. is indicative of a[38-40]

$$^1T_A \rightsquigarrow {}^1T_P \qquad 1.6$$

intermolecular transfer, where ^1T_P the first excited triplet state of the polymer and ^1T_A, is that for the additive.

It can be simply assumed that the radiative rate constant, k_r, for the process: $^1T \longrightarrow {}^oS$ is temperature independent. And the non-radiative rate constant, k_{nr}, is temperature dependent.

Graves, Hoffman and McGlynn[39] found that the phos. life-time (τ_p) for a range of aromatic species in PMMA and at a wide range of temperature is given by:

$$\frac{1}{\tau_p} = k_r + k_{nr} + k_{et}\,[{}^oS_P] \qquad 1.7$$

where:

k_{et} = rate constant for triplet-triplet energy transfer process.

k_{nr} can be expressed as[40-42]:

$$k_{nr} = {}^{o}k_{nr} + {}^{'}k_{nr} \exp^{(-\Delta E_{nr}/kT)} \qquad 1.8$$

and since $[{}^{o}S_p]$ is constant, k_{et} may be written as:

$$k_{et} = {}^{'}k_{et} \exp^{(-\Delta E/kT)} \qquad 1.9$$

where ${}^{o}k_{nr}$, ${}^{'}k_{nr}$ and ${}^{'}k_{et}$ are independent of temperature, and ΔE_{nr} and ΔE_{et} are the activation energies for the non-radiative and energy transfer processes respectively. The general equation can be written as:

$$\frac{1}{\tau_p} = k_r + {}^{o}k_{nr} + {}^{'}k_{nr} \exp^{(-\Delta E_{nr}/kT)} + k_{et}[{}^{o}S_p] \times \exp^{(-\Delta E_{et}/kT)} \qquad 1.10$$

As in the case of many workers[38,43] the curves generated may be fitted by two temperature-dependent processes as given in equation (1.10).

Of these two processes, one is dominant at low temperature, and characterized by a low activation energy associated with ΔE_{nr}. The second process dominates at higher temperature, with a much larger activation energy and associated with ΔE_{et}. Results showing similar conclusions have been obtained in these laboratories[44].

(VI) Quenching of excited states

A substance which accelerates the decay of an electronically excited state to ground state or to lower level is described as a

quencher[17]:

$$^{*}S + Q \longrightarrow {}^{o}S + Q \qquad 1.11$$

The process is of such generality that it occurs by many different mechanisms (Figure 1.4). Also it can be induced by many different substances, of these oxygen is the most efficient quencher for both singlet and triplet excited states.

(1) Quenching by oxygen

To understand the mechanism of the quenching process of excited states of aromatics by oxygen, fundamental information concerning the generation and properties of singlet oxygen needs to by discussed.

(A) Singlet oxygen

Molecular oxygen is a triplet in the ground state, and is therefore paramagnetic. Above its ground state there are two excited singlet states the properties of which are listed in Table 1.3[92-94].

Table 1.3

Properties of singlet oxygen

State of O_2	configuration of electrons in highest occupied M.O.S.	Relative energy ($kJ\ mole^{-1}$)	lifetime in liquid
Ground state, $O_2(^{3-}\Sigma_g)$	↑ ↑	0	
First excited state, $O_2(^{1}\Delta_g)$	↓↑ —	93.6	$\sim 10^{-4}$ S
Second excited state, $O_2(^{1}\Sigma_g^{+})$	↑ ↓	156	$\sim 10^{-10}$S

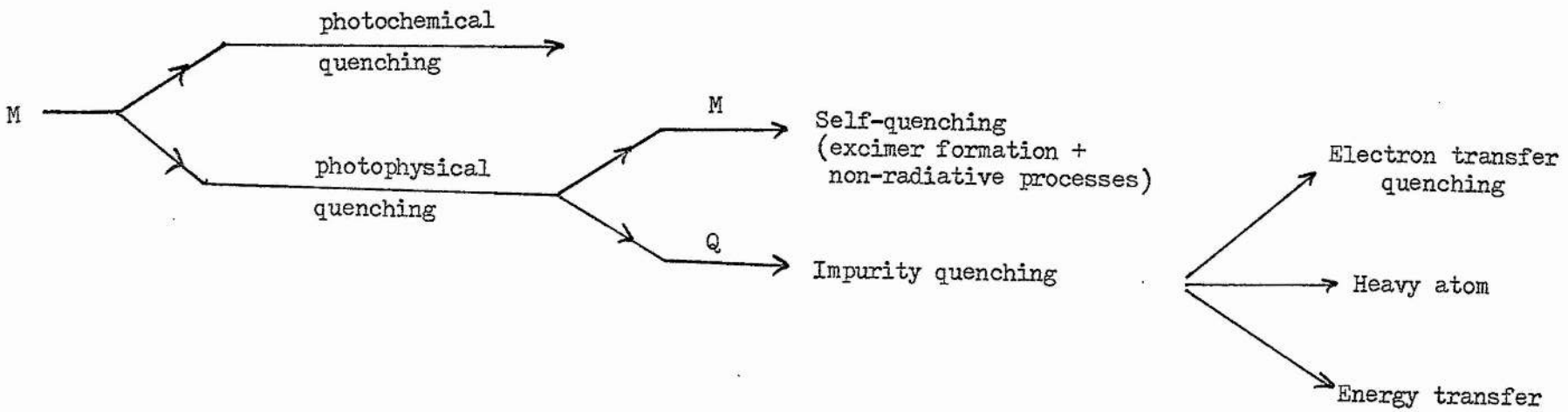


Figure 1.4

Quenching processes.

The very short life-time of $O_2(^1\Sigma_g^+)$ can be accounted for by the fact that the conversion $O_2\ ^1\Sigma_g^+ \longrightarrow O_2\ ^1\Delta_g$ is spin allowed whereas $O_2\ ^1\Delta_g \longrightarrow O_2\ ^3\Sigma_g^-$ is spin forbidden. Thus $O_2\ ^1\Sigma_g^+$ most probably returns to the ground state via $O_2\ ^1\Delta_g$. Some properties of $O_2\ ^1\Sigma_g^+$ in the gas phase have been reported[95], but there is no convincing evidence for any chemical reaction involving this form in solution. Many workers believe the only excited state of oxygen relevant to liquid and solid state chemistry is $^1\Delta_g$[96,97], and will be denoted $^1O_2$. The emission peak from the process[98]:

$$^1O_2 \longrightarrow {}^3O_2 + h\nu\ (636\ nm) \qquad 1.12$$

is commonly used for the detection of $^1O_2$ state.

(B) Generation of $^1O_2$.

There are three methods available for generating $^1O_2$:

(i) physical (microwave discharge treatment of O_2^3),

(ii) chemical,

(iii) photo-sensitisation.

Of the three techniques only the last has any relevance to this work. Singlet oxygen is formed in the reaction between molecular oxygen and a sensitizer molecule (S) in its singlet or triplet excited state[13,99-102]. The following mechanisms for sensitizer quenching are allowed based on energy considerations:

(a) For the excited singlet state of a sensitizer:

$$^1S + {}^3O_2 \longrightarrow {}^1T + {}^1O_2 \qquad 1.13$$

or

$$^1S + {}^3O_2 \longrightarrow {}^oS + {}^1O_2 \qquad 1.14$$

(b) For the triplet state of a sensitizer:

$$^1T + {}^3O_2 \longrightarrow {}^oS + {}^1O_2 \qquad 1.15$$

Kearns and co-workers[103,104] found that $^1O_2$ molecule in its ground state may be formed when the excitation energy of the sensitizer molecule exceeds 93.6 kJ mole^{-1}. It has been found that $^1O_2$ is more likely to be generated by the triplet excited state rather than the singlet excited state of the sensitizer[105-107].

Aromatics and dyes are the most important molecules which satisfy the energy condition for generating singlet oxygen, a process which Khan postulated[93] and Snelling found[108] to proceed by energy transfer mechanism.

It is worth noting that the quenching of singlet state seems to occur by the following mechanisms:

$$^1S + {}^3O_2 \longrightarrow {}^1T + {}^3O_2 \qquad 1.16$$

this is the dominant process in low viscosity solutions, and

$$^1S + {}^3O_2 \longrightarrow {}^oS + {}^3O_2 \qquad 1.17$$

is dominant in viscous and rigid solutions, and

$$^1S + {}^3O_2 \longrightarrow {}^1T + {}^1O_2 \qquad 1.13$$

is only energetically possible if ΔE_{ST} energy gap exceeds the $^1O_2$ excitation energy[71] e.g. naphthalene. It is found that quenching of ^1T by $^3O_2$ and yielding $^1O_2$ (1.15)[109] is more efficient by factor of $\sim 10^3$ than the[93]:

$$^1T + {}^3O_2 \longrightarrow {}^oS + {}^3O_2 \qquad 1.18$$

Thus it can be seen that quenching of excited states by O_2 is closely related to the generation of singlet O_2.

(2) Quenching by nitric oxide "NO"

Nitric oxide molecule is also a paramagnetic at room temperature. It has unpaired electrons and is an electron acceptor. In the ground state it may interact with an excited aromatic molecule in a similar manner to oxygen (e.g. quenching triplet and singlet excited states). The lowest excited state of NO is at 450.9 kJ $mole^{-1}$, which exceeds the triplet and almost the singlet excitation energies of the aromatic hydrocarbons[93]. Hence no processes analogous to:

$$^1T + {}^3O_2 \longrightarrow {}^oS + {}^1O_2$$

can occur with NO which acts simply as a paramagnetic species. It is found that the rate constant for quenching the triplet excited state of aromatics in solution from 77 K to 293 K by O_2 is about 10-20 times higher than that for NO. Thus NO is a less effective quencher than O_2, since NO quenches only by enhanced intersystem crossing, whereas O_2 also quenches by energy transfer for which the rate constant is very large[110]. This observation provides further indirect evidence for process 1.15[111].

(3) Quenching by DABCO and cyasorb 1084

Of the amines, DABCO is moderately effective as an $^1O_2$ quencher[112-114] and singlet states[113] in solution.

Paramagnetic nickel (II) complexes (e.g. cyasorb 1084) which are

used as a commercial photostabilizers of polymers, have been shown to quench the triplet of benzophenone[115] and singlet O_2[116,118] in dilute solutions. The observed efficiency of quenching is less than that of diamagnetic square-planar nickel (II) complex. Harper and McKellar[117] emerged with the same conclusion in studies of both polymer stability and triplet quenching in Pst films. The mechanism of the quenching of triplets by nickel photostabilizers is thought to be due to electronic energy transfer.

(4) Kinetics of quenching

Kinetics are basic to any real understanding of quenching phenomena. The mechanism for the formation and deactivation of an excited molecule is shown in Table 1.4:

Table 1.4

The deactivation mechanism of excited states

Step	Reaction	Rate
Absorption	$^{o}S + h\nu \longrightarrow {}^{1}S$	I_a
Fluorescence	$^{1}S \longrightarrow {}^{o}S + h\bar{\nu}$	$k_1 [{}^{1}S]$
Quenching with energy transfer	$^{1}S + Q \longrightarrow Q + {}^{o}S$	$k_q [{}^{1}S][Q]$
Deactivation	$^{1}S \longrightarrow {}^{o}S + \text{heat}$	$k_d [{}^{1}S]$

at equilibrium, i.e. during steady-state illumination

$$\frac{d\,[{}^{1}S]}{dt} = I_a = [{}^{1}S](k_1 + k_d + k_q[Q]) = 0 \qquad 1.19$$

Thus,

$$[^1S] = \frac{I_a}{k_1 + k_d + k_q[Q]} \qquad 1.20$$

and the quantum yield, Q_f, from excited molecules is:

$$Q_f = \frac{k_1 [^1S]}{I_a} = \frac{k_1}{k_1 + k_d + k_q [Q]} \qquad 1.21$$

and in the absence of quencher:

$$^oQ_f = \frac{k_1}{k_1 + k_d} \qquad 1.22$$

By dividing equation (1.22) by equation (1.21) the following expression is obtained:

$$\frac{^oQ_f}{Q_f} = \frac{k_1 + k_d + k_q [Q]}{k_1 + k_d}$$

$$= 1 + \frac{k_q}{k_1 + k_d} [Q] \qquad 1.23$$

but

$$\tau_f = \frac{1}{k_1 + k_d} \qquad 1.24$$

Substitution of equation (1.24) into equation (1.23) gives the well known Stern-Volmer equation[119]:

$$\frac{^oQ_f}{Q_f} = 1 + \tau_f k_q [Q] \qquad 1.25$$

In photochemical studies and under ideal conditions a straight line is obtained when $^{o}Q_f/Q_f$ is plotted vs. $[Q]$ as depicted in fig. 1.5a.

(5) Anomalies in the Stern-Volmer plot:

A few anomalies in the Stern-Volmer plot have been observed. Within the scope of this work, the most important is when both excited singlet and triplet states are inter-dependent and both are quenched, in this case the quenching curve may take a different form see Fig. 1.5b.

In 1969, Shetlar[120] proposed a method to solve this problem by distinguishing between the excited singlet and the triplet contribution in solution. Another anomaly was considered by Sheltar[120], when a part of incident radiation can be observed by the quencher at high concentration see Fig. 1.5c.

The values for k_q, the quenching rate constant for singlet and triplet quenching will be discussed in the final chapter of this thesis.

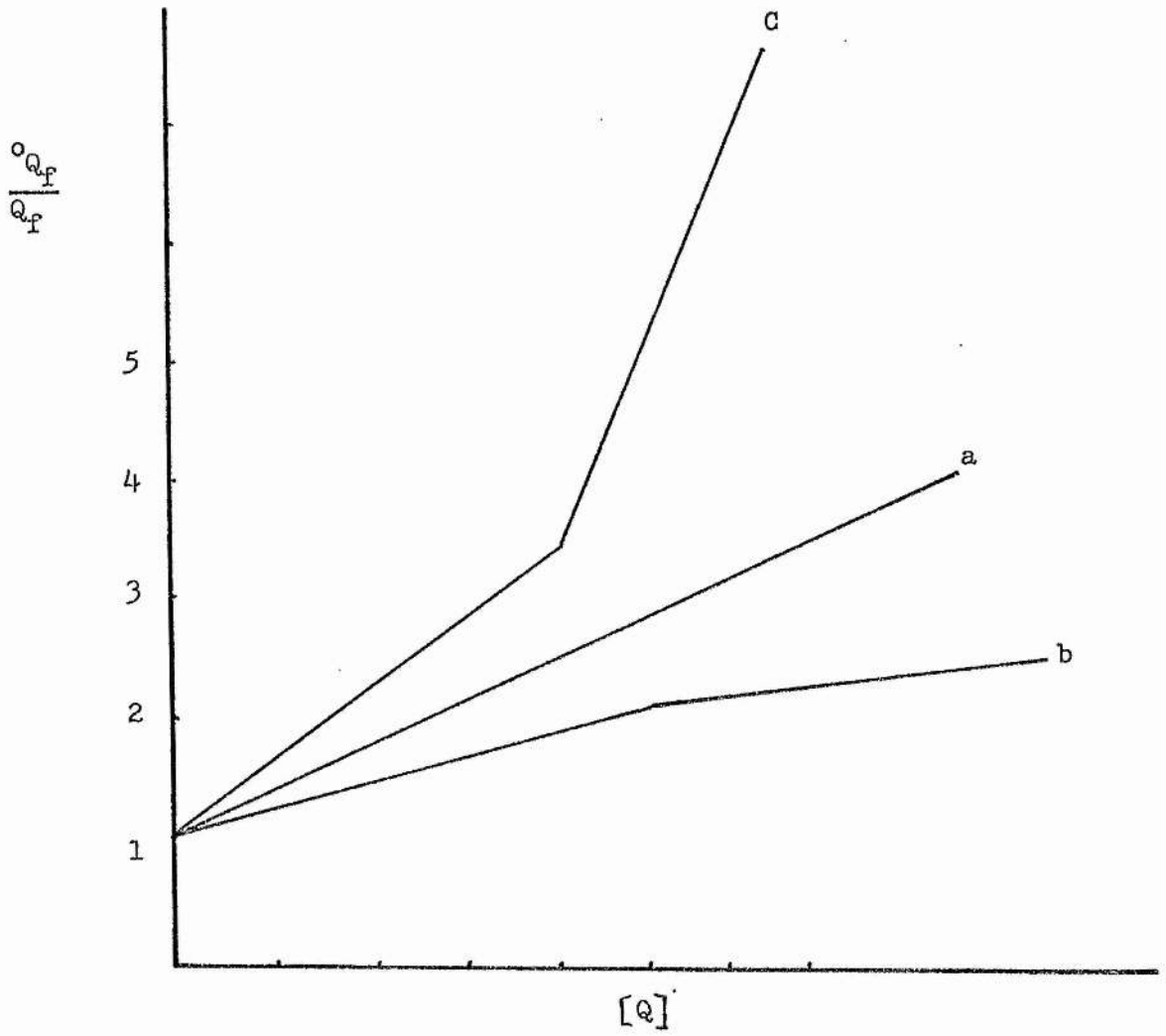


Figure 1.5

Typical and anomalies in Stern-Volmer plot.

CHAPTER 2

EXPERIMENTAL

1. Materials

A. Solvents

The solvents used methanol, ethanol, cyclohexane, toluene, benzene, dichloromethane and dichloroethane were of Analar grade and were redistilled under reduced pressure. The middle fraction was retained.

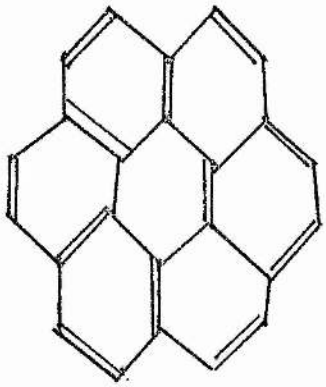
B. Additives and quenchers

Molecules used were naphthalene (N); perylene (P), coronene (COR); triphenylene (Tri); DABCO (1,4-diazabicyclo 2,2,2 octane $N(CH_2-CH_2)_3N$ and cyasorb 1084 [2-2-Thiobis(4-2-octylphenolato)-n-butylamine]nickel-II. Naphthalene was purified by sublimation. The others were used as supplied without additional purification. Where possible the purest form of a compound was used. Purity of a given sample was checked by measuring its excitation/emission spectra and comparing it with known published spectra. A sample was considered impure if its emission spectrum varied with exciting wavelength[13].

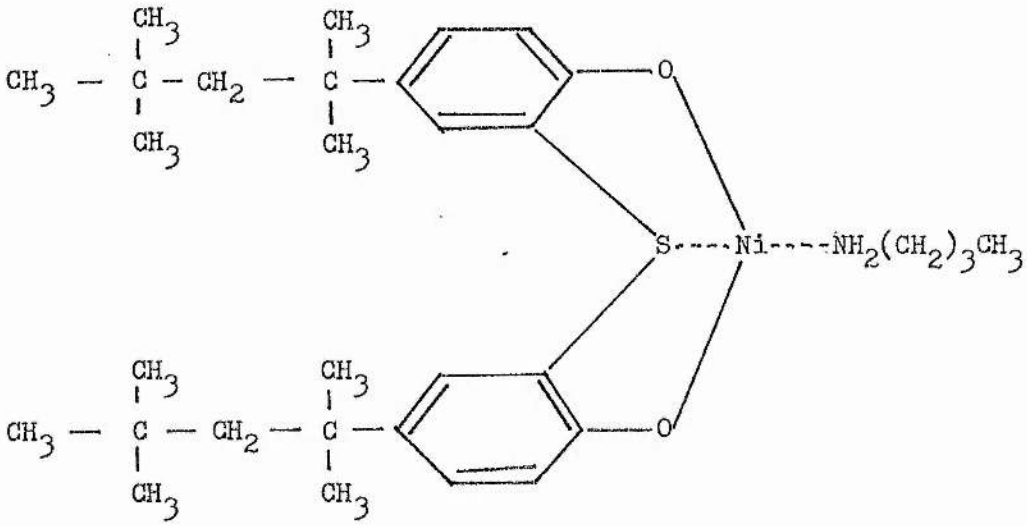
Oxygen and oxygen-free-nitrogen were obtained from the British Oxygen Company Ltd. and were dried before use. The structure of some additives are shown in figure 2.1.

C. Polymers

Styrene (St), methylmethacrylate (MMA), ethylmethacrylate (EMA) and vinylacetate (VA) monomers were purified by treatment with sodium hydroxide solution and washed several times with distilled water. Then they were dried over anhydrous magnesium sulphate and fractionally distilled under nitrogen atmosphere. The middle



Coronene



Cyasorb 1084

Figure 2.1

Chemical structure of some additives,

fraction of each distillation was collected and stored below room temperature until required.

(i) Polystyrene (Pst), Polymethylmethacrylate (PMMA) and their co-polymers (St-MMA)

Styrene was polymerized by free radical polymerization in vacuum using azo-iso-butyro-nitrile (AZBN) as initiator. The solution of the monomer and the initiator was sealed under vacuum in a glass tube after several freeze-pump-thaw cycles, kept at 60°C for six days, followed by one day at 100°C. The polymer was purified by dissolving in dichloroethane, then reprecipitated from agitated methanol, and filtered. This was repeated twice to remove traces of monomer and initiator. The polymer was dried in a vacuum oven for two weeks at approximately 55°C.

PMMA and a series of (St-MMA) copolymers (maximum styrene content 80%) were prepared and purified by the above procedure. Another set of (St-MMA) copolymers was prepared under air. Commercial PMMA, PVA and Pst were also used and they were purified and dried as above before use. Head-head Pst, Rxmst and (St-αmst) block copolymer (gifted by Dr. D.H. Rudkin) and high molecular Pst ($MW > 10^7$) (gifted by Dr. G.G. Cameron) were used without further purification.

(ii) Polyethylmethacrylate (PEMA) and ethylmethacrylate-methylmethacrylate (E-M) co-polymers

PEMA, (E-M) 20% and (E-M) 60% copolymers were prepared under vacuum, then purified as described earlier (i). The monomer mixture was as stated and conversion was 100% thus the overall composition of the copolymers was that of the monomer mixture.

Infra-red and ultra-violet absorption spectra as well as

^{1}H.N.M.R. analysis and microanalysis were used to determine the composition of the polymers.

2. Preparation of films

Since highly-fluorescent molecules can be detected at concentrations as low as 10^{-10} M[124], so an attempt was made, as far as possible, to maintain a high standard of purity in sample preparation and when monitoring fluorescence and phosphorescence spectra.

Clear uniform films, (30-60) μ in thickness were cast as follows. Two ceramic tiles, one on the top of the other, were floated on mercury contained in a glass bath. Then a solution of polymer, with or without additive, was laid on the surface of the upper tile. The system then covered by a watch glass. After slow evaporation of the solvent the films were removed and dried in a vacuum oven at 55°C for at least two weeks.

The thickness of the films, which were required for diffusion measurements, was calculated by knowing the weight, area and density of any given sample. Densities were taken as 1.23, 1.05, 1.1215 and 1.169 gm/cm^3 for PMMA[121], Pst[121] PEMA[122] and PVA[122] respectively.

The density of any co-polymer was calculated from the combination of the densities of the pure polymers in the ratio of the copolymer composition.

3. Instruments

Ultra-violet and visible spectra were recorded on a Perkin-Elmer 402 Spectrophotometer. Infra-red spectra were recorded on a Perkin-Elmer 257 Grating Spectraphotometer. All ultra-violet and infra-red spectra of films were run with air as reference.

^{1}H.N.M.R. spectra were obtained using a Varian HA 100 100MHz N.M.R. Spectrophotometer.

Luminescence studies were performed on a Perkin-Elmer Spectrophotometer, Model MPF-2A. A fuller description of the instrument and its range of application will be given in the next section.

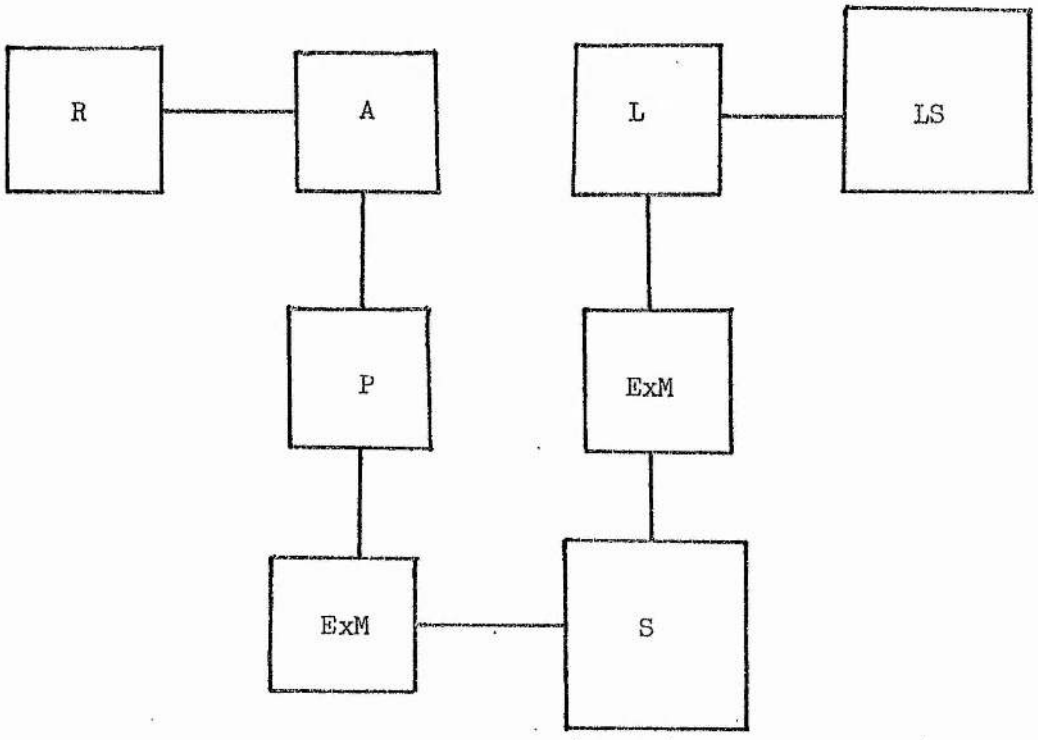
4. Fluorescence, phosphorescence and polarisation measurements

a. Model MPF-2A Spectrophotometer

The MPF-2A fluorescence spectrophotometer is designed for the measurement of excitation and emission spectra. In this work it was used for emission studies only. The principles of the instrument are best outlined in a block diagram as shown in figure 2.2.

Figure 2.2

Perkin-Elmer Spectrophotometer, Model MPF-2A



The instrument consists of a spectrophotometer, a power supply for the lamp source, LS, an amplifier, A, and a recorder, R. The spectrophotometer includes two grating monochromators, one for irradiating a specimen in the sample compartment, S, with monochromatic light from a 150 watt xenon source, L, in the range 200-700 nm (excitation monochromator, ExM), and the other for permitting selective measurements on the intensity of the light emitted by the sample in the range 220-800 nm, (emission monochromator, EmM).

Light from the xenon source passes into the excitation monochromator where it strikes a beam splitter before dispersion. The portion of the beam which is not deflected by the splitter is dispresed in the excitation monochromator and light from this monochromator is focussed on the sample. Emitted light from the sample is directed to the emission monochromator where it is dispersed.

The dispersed emitted light strikes the sample photomultiplier, P, to produce a signal which is proportional to the intensity of the emitted light. This signal then passes through the amplifier and is recorded.

(b) Instrument Accessories

In the work reported in this thesis four instrument accessories were employed for use with fluid and rigid media.

(i) Sample holder for solutions

This compartment and its holder were designed for fluorescence studies in solutions (figure 2.3). This sample holder and its brass base were removed and the sample holder for films, which will be described in the next section, was installed.

(ii) Sample holder for films

The sample holder was a U.V.-quartz cell, 1mm in thickness.

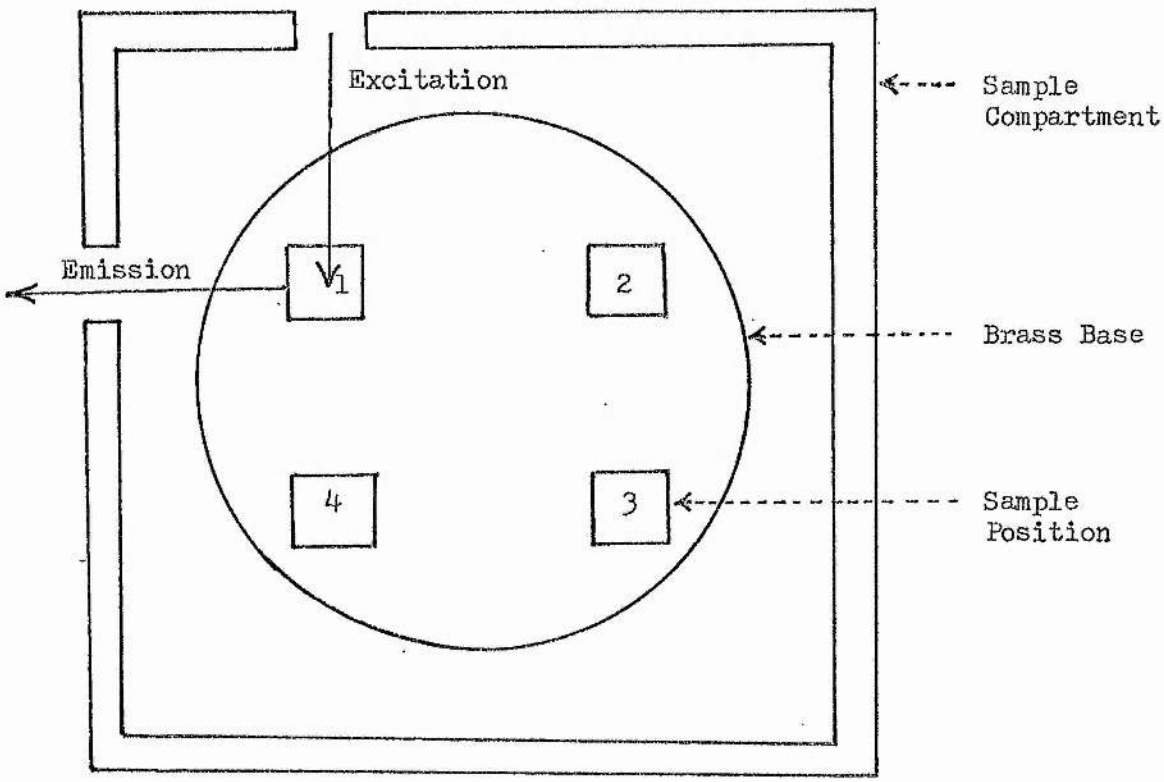


Figure 2.3

Rotatable cell holder accessory for solution

It was joined to a glass tube, fitted with a B 14 cone, making the total length 14 cm. A polymer film was inserted into the quartz part of the holder and positioned inside the spectrofluorimeter which in turn was connected to the vacuum line. The exciting light impinges on front face of the cell, and the emitted light from the back face of the cell was measured at 90° to the exciting beam.

The holder was securely clamped because the amount of radiation incident upon the sample surface varied when the distance between the instrument lens and the sample varied. Attempts were made to reduce the scattering of light as much as possible. It was necessary to reduce the light in the laboratory to eliminate light leaking into the monochromator. The current was stabilized by a constant voltage transformer and, moreover, the measurements were taken after the instrument had been switched on for a few hours to ensure that the light intensity became constant.

This technique made it possible to carry out measurement over the wide range of temperatures from $120^{\circ}C$ down to temperature of boiling nitrogen, and in vacuum (about 1.33×10^{-3} Nm^{-2}) and under oxygen pressures up to 9.33×10^{4} Nm^{-2}.

(iii) Variable temperature accessory

For a measurement, the sample holder described in (ii) was positioned inside a quartz dewar flask, 12 cm in height by 3 cm in diameter. The flask was heated by a Henly resistance heater controlled by a variac. Temperature was monitored using a Nickel/Chromium-Nickel/Aluminium thermocouple connected to a Digitron 175 electronic thermometer.

Both the heater and thermocouple were positioned so as not to interrupt the light beam, as shown in figure (2.4). The top of the

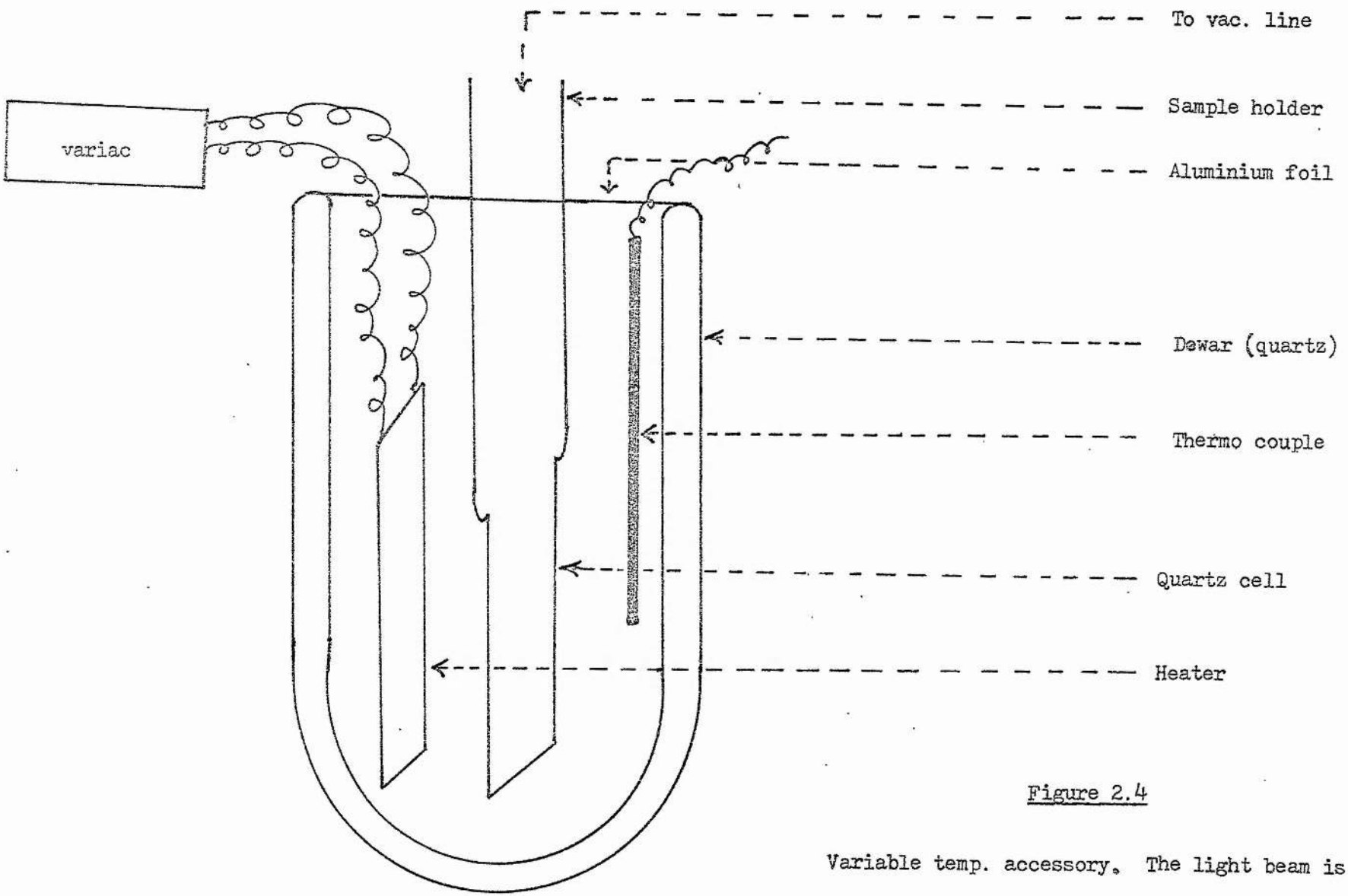


Figure 2.4

Variable temp. accessory. The light beam is directed perpendicular into the plane of the paper.

flask was covered with aluminium foil to ensure good temperature control. The temperature of the system was allowed to stabilize before proceeding, usually 30 minutes, and remained constant to within $\pm$ 0.1°C of the stated temperature.

For measurements at low temperature the dewar flask was filled with an ice and water mixture (0°C), dry ice and acetone mixture (-80°C) and with liquid nitrogen (-196°C).

(iv) Polarization Accessory

This modification of the sample compartment was used in conjunction with (ii) and (iii) above. Two polarizers were mounted in the sample compartment, one in the excitation beam before it strikes the sample and the second in the fluorescence beam before entering the emission monochromator (Figure 2.5). In order to measure the polarization of fluorescence or phosphorescence, P, the sample was excited by the vertical component from the excitation monochromator and the vertical and horizontal component of the fluorescent light were measured, I_{vv} and I_{vh} respectively.

P, by definition is

$$P = \frac{I_{vv} - I_{vh}}{I_{vv} + I_{vh}} \qquad 2.1$$

However, a correction to P is necessary because the intensities are measured after the emission monochromator grating where dispersion occurs.

The ratio of the recorded intensities after dispersion, I_{hv}/I_{hh}, is termed the grating transmission factor, G. Thus I_{vv} and I_{vh} are modified by I_{hh} and I_{hv} which gives the correction to P.

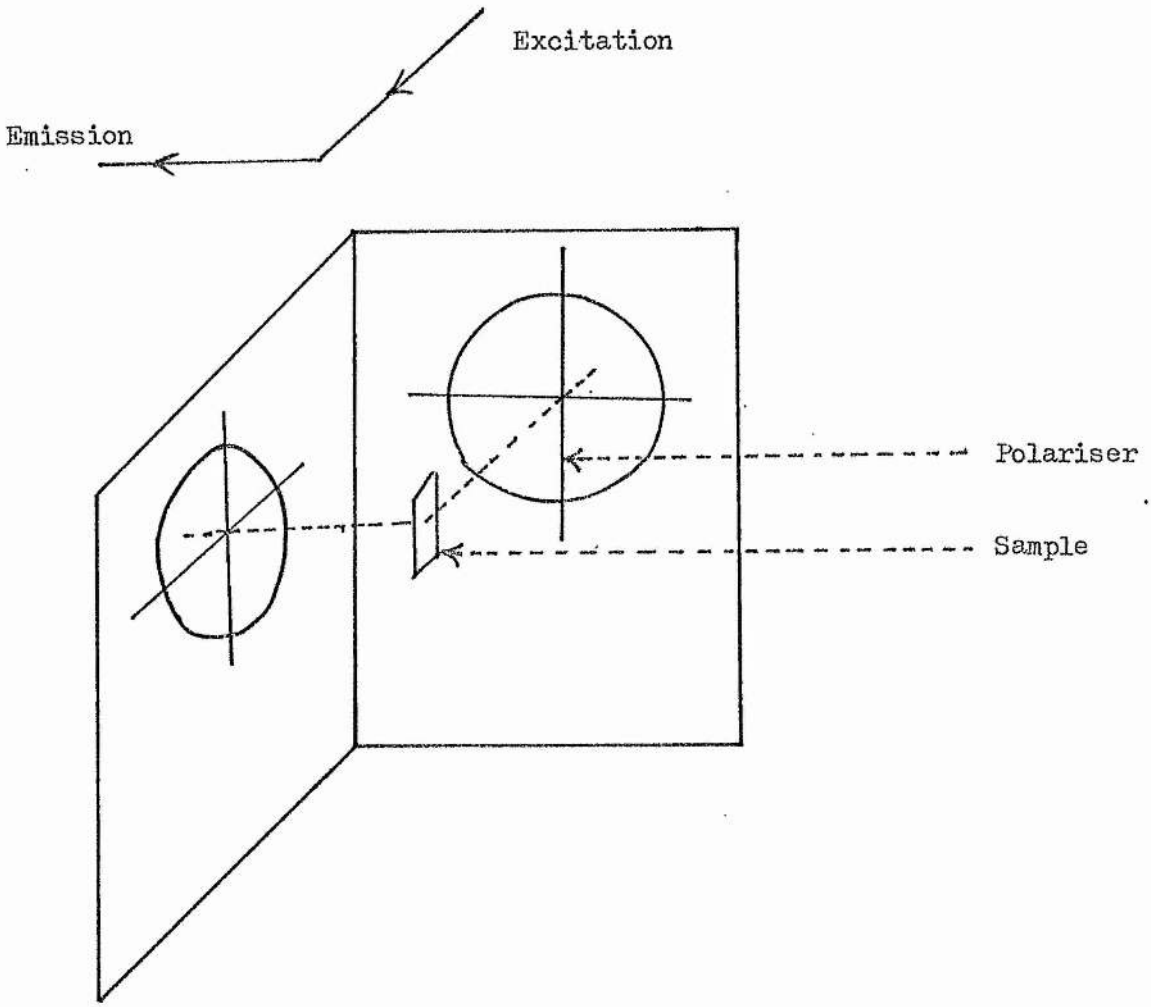


Figure 2.5

Polarisation Accessory

Thus

$$P = \frac{I_{vv} - G\, I_{vh}}{I_{vv} + G\, I_{vh}} \qquad 2.2$$

The polarizers were set to the position indicated in Table (2.1) and P evaluated from the above equation (2.2).

Table (2.1)

Determination of, P

Component in excitation beam	Excitation Polarization	Emission Polarizor	Component in emission beam
Horizontal	90	0	I_{hv}
Horizontal	90	90	I_{hh}
Vertical	0	0	I_{vv}
Vertical	0	90	I_{vh}

5. Measurements

(a) Quenching by oxygen gas

The general arrangement of the experimental procedure was:

1. The sample holder with the film was positioned inside the spectrofluorimeter and connected to the vacuum line as described previously. Fluorescence intensity was recorded automatically in vacuum after the sample had been pumped out for 12 hours at least, and after as short a time of irradiation as possible in order to

reduce any photochemical effect.

2. The excitation shutter and the tap between the vacuum line and the sample holder were closed. About 1.33×10^{3} Nm^{-2} or less of oxygen gas was carefully admitted to the system which was then left in the dark for 10-15 minutes to reach a state of equilibrium. It has been shown in diffusion work that it takes about 3 minutes for oxygen to diffuse into the polymer film[123]. The fluorescence intensity was measured after the sample had been irradiated for a short time.

3. Step number 2 was repeated at different oxygen pressures up to 9.33×10^{4} Nm^{-2}.

A travelling microscope was used to accurately measure the pressure of oxygen, which was dried by passing through a silica gel column.

Since many factors could affect the result, every quenching experiment was repeated many times. The result was accepted to be correct if the results agreed after each successive run. Many experiments were neglected because they did not satisfy this condition.

For solution work, the sample holder for solution had to be taken out every time in order to change the quencher concentration. At the beginning of each experiment the scattering light was measured. The first value was used as a standard to correct the fluorescence intensity at different concentrations of quenchers.

(b) Measurements of fluorescence, phosphorescence and phosphorescence decay

These measurements were automatically recorded as follows. The spectrofluorimeter was connected to a data transfer unit (d.t.u.)

to record the intensity at selected time intervals on paper tape. This arrangement allowed the output voltage to be sequentially sampled at intervals of $\gg$ 0.33 sec. To record phosphorescence decay the excitation and emission monochromators were set to the appropriate wavelengths. The voltage was then recorded at predetermined intervals after closing the excitation shutter. This method allowed accurate measurement of the decay curves of samples with "life-times" $>$ 2 sec. Phosphorescence lif-time was calculated by computer programme or by a graphical method.

The procedure using thin films and pumping-out the system for a long time, is considered to allow removal of all mobile quenching agents such as oxygen, monomer, or residual solvents. For this reason a relatively long phosphorescence life-times were obtained in this work for aromatics at room temperature as we shall see in the next chapter.

CHAPTER 3

Results

I Polymer characterisation

Before considering the nature of the experimental results it is necessary to establish the composition of the St-MMA co-polymers.

1. Composition

A series of copolymers were examined with styrene mole fraction of 20%, 40%, 60% and 80%. These compositions were based on ^{1}H.N.M.R. and microanalysis determination. ^{1}H.N.M.R. spectra were recorded at 60°C in deutrochloroform. Good agreement between the two methods was obtained as shown in Table 3.1.

Table 3.1

Microanalysis and ^{1}H.N.M.R. analysis for St.MMA copolymers

Theoretical	^{1}H.N.M.R. analysis	Microanalysis
20%	18.8	22.8
40%	38.1	37.13
60%	58.07	58.9
80%	78.64	78.52

2. Emission spectra

Emission of polystyrene in the copolymers was studied in solution and in thin films. Fluorescence spectra for Pst in different St.MMA

copolymers solutions are shown in figure 3.1. A solution of (St-MMA) 40% copolymer in methylene chloride did not show excimer emission even at high concentration (10^{-2}M in styrene repeat unit). From that we can conclude there is no inter- or intra-molecular excimer for this styrene content in solution. On the other hand, a thin film of the same copolymers showed an intense excimer emission, a point which indicates that the formation of inter- or intra-molecular excimer is more likely in films rather than in solution, probably inter-molecular. The variation in the $I_{excimer}/I_{monomer}$ ratio for polystyrene was investigated using (St-MMA) 60% copolymer film, at room temperature and at 77K. Figure 3.2 shows that there is a remarkable decrease in excimer intensity at 77K. Films of polystyrene and (St-MMA) copolymers, prepared in vacuum and carefully purified, exhibited "anomalous" fluorescence at 324, 355, 375 and at 384 nm at room temperature. Meanwhile the usual emission was observed from their solutions in methylene chloride.

Both monomer and excimer fluorescence have been observed from Pst solution. Thin film of Pst showed mainly excimer emission at room temperature, and both monomer and excimer at 77K.

Our investigations have observed acetophenone type phosphorescence at room temperature and at 77K from Pst and its copolymers with MMA prepared in vacuum or in air. The phosphorescence decay observed at 430 nm at 77K was found to be non-exponential, and its life time at long decay lines was measured and found to be 4.27 sec. in Pst and 3.71, 2.15 and 2.07 sec. in 80%, 60% and 20% styrene content in (St-MMA) copolymers respectively.

II. Quenching of the excited states of aromatics in polymers

The excited states of aromatic hydrocarbons, triphenylene,

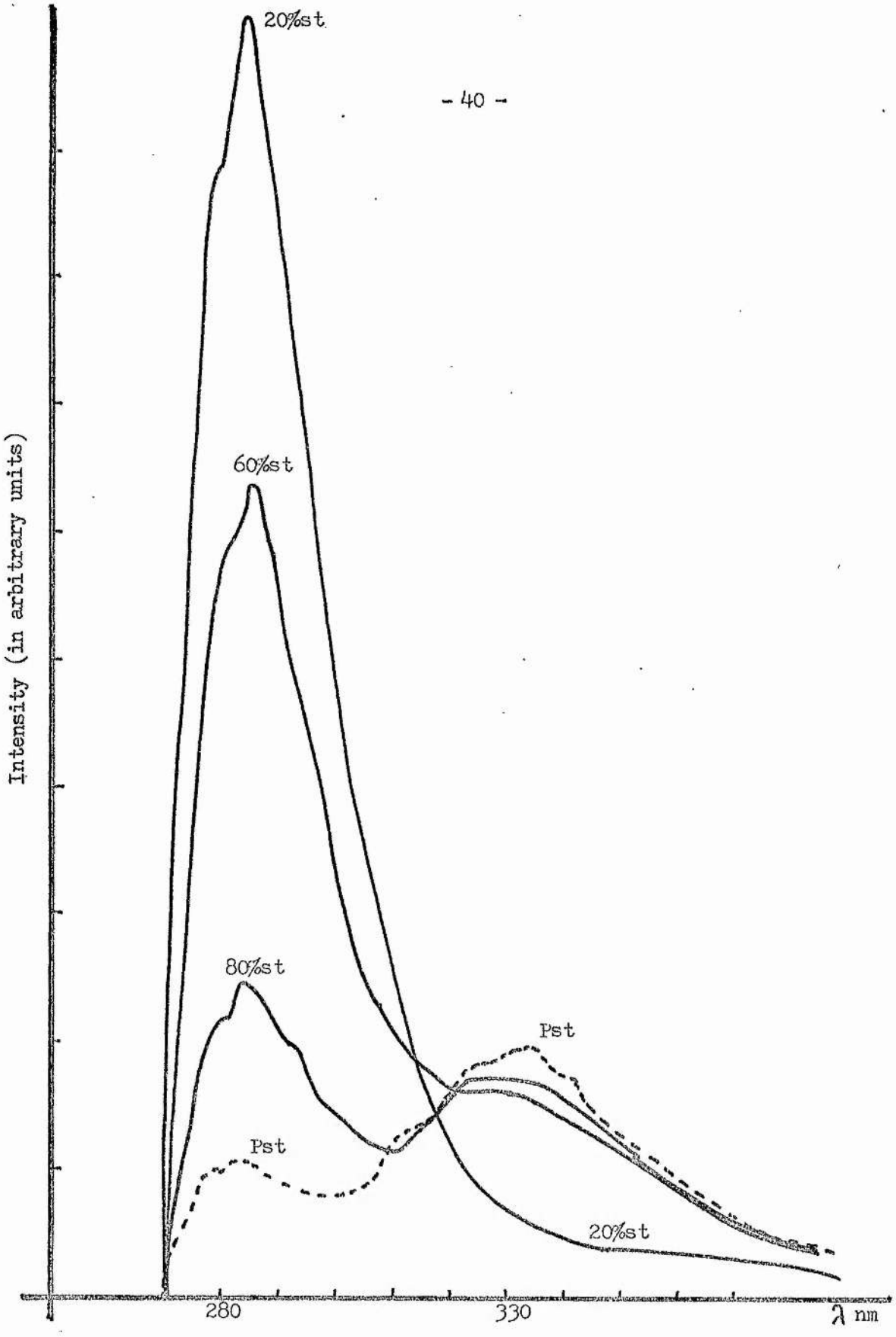


Figure 3.1

Fluorescence of Pst in different st-MMA co-polymers, 0.5 gm/l solution in CH_2Cl_2. Excitation at 260 nm.

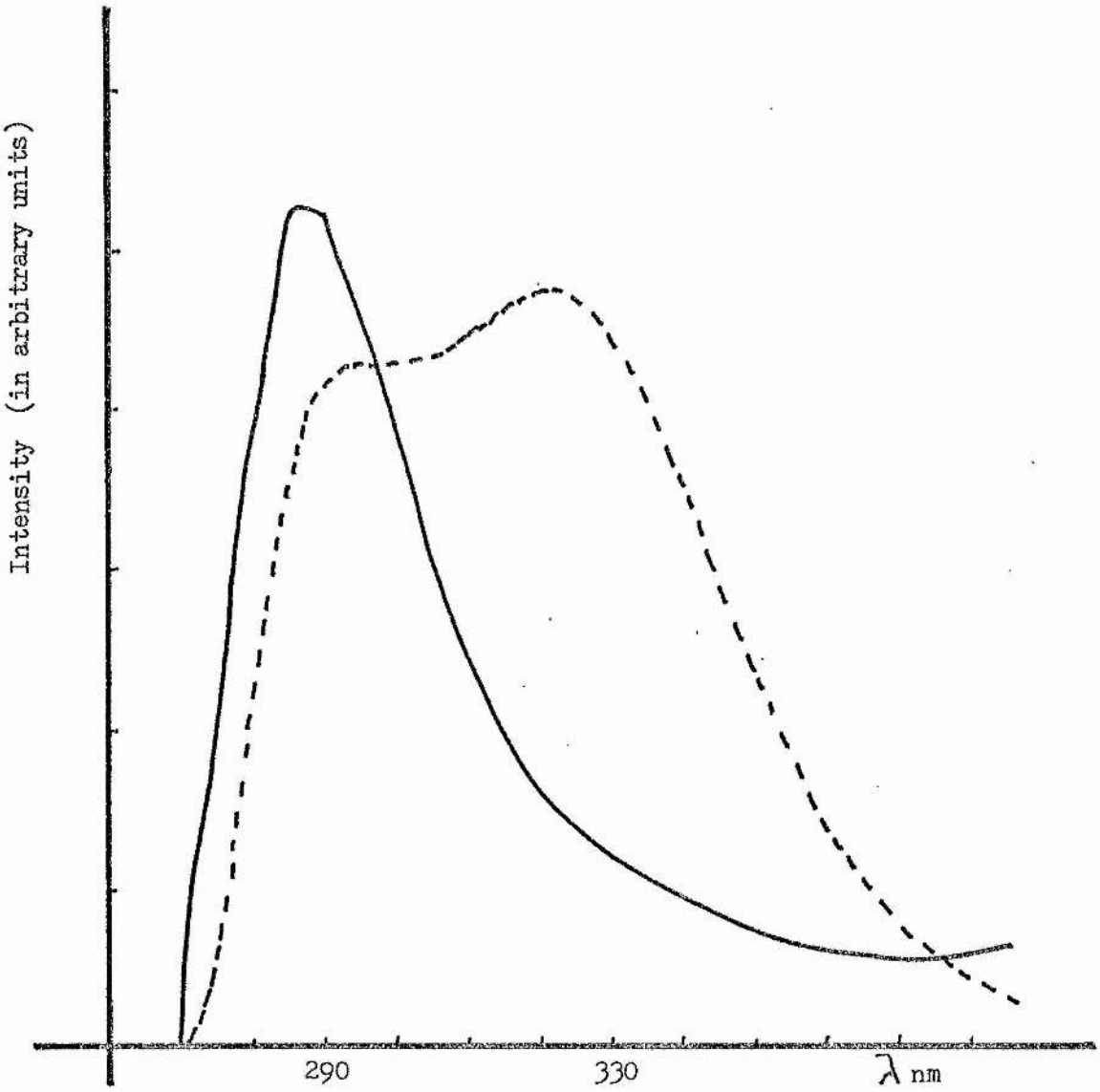


Figure 3.2

Uncorrected spectra for Pst Fluorescence in (St-MMA) 60% co-polymer film, at 77K (——) and at R.T. (---).

coronene, phenanthrene, naphthalene and perylene were investigated in different plastics and under different conditions, using mobile and fixed quenchers. Unless stated, all the work was carried out on additives in polymer films 30-60μ thick, with concentration of the order 10^{-4} M. The excited state of polystyrene was also studied. This chapter can be conveniently divided into different parts according to the substances investigated, beginning with triphenylene.

1. Triphenylene

Triphenylene has an intense phosphorescence with an exeptionally long lifetime at room temperature. For this reason much work has been carried out on it in different plastic media, and especially in PMMA matrix.

A. Triphenylene in PMMA

A dry, clean piece of film of this sample was inserted into the sample holder, put inside the spectrofluorometer, and the whole apparatus then connected to the vacuum line, as mentioned previously. The system was pumped out to high vacuum for two days and the following results were obtained.

i. Figure 3.4 shows the total emission spectrum for the compound. It can be seen that the phosphorescence at 466 nm is so intense that it exceeds the fluorescence. The intensities of phosphorescence and fluorescence were measured at 466 nm and 356 nm respectively. The ratio Q_p/Q_f for triphenylene will be proportional to I_p/I_f and comparison can be made provided measurements are always made at the same wave-lengths. The ratio I_p/I_f was measured and found to be 1.5 and $\sim$ 3 at room temperature and at 77K respectively, when the sample was excited at 270 nm.

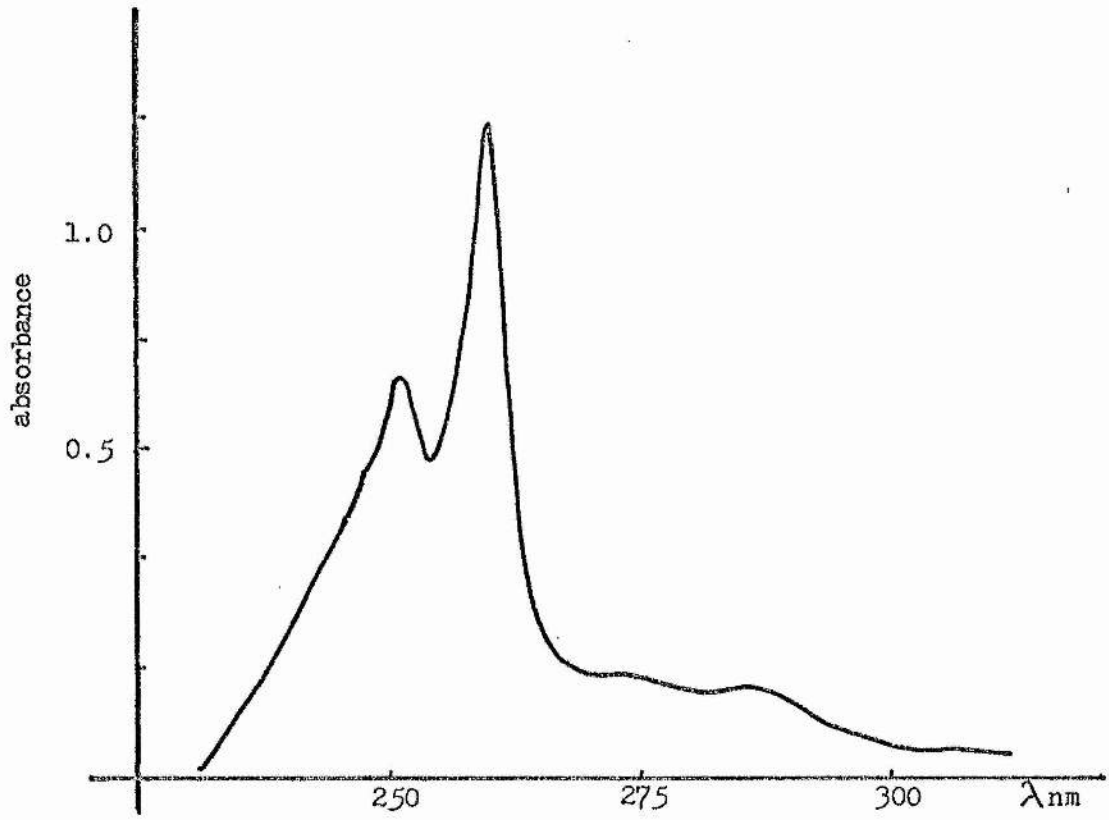


Figure 3.3

Absorption spectrum for triphenylene 10^{-4} M in PMMA film.

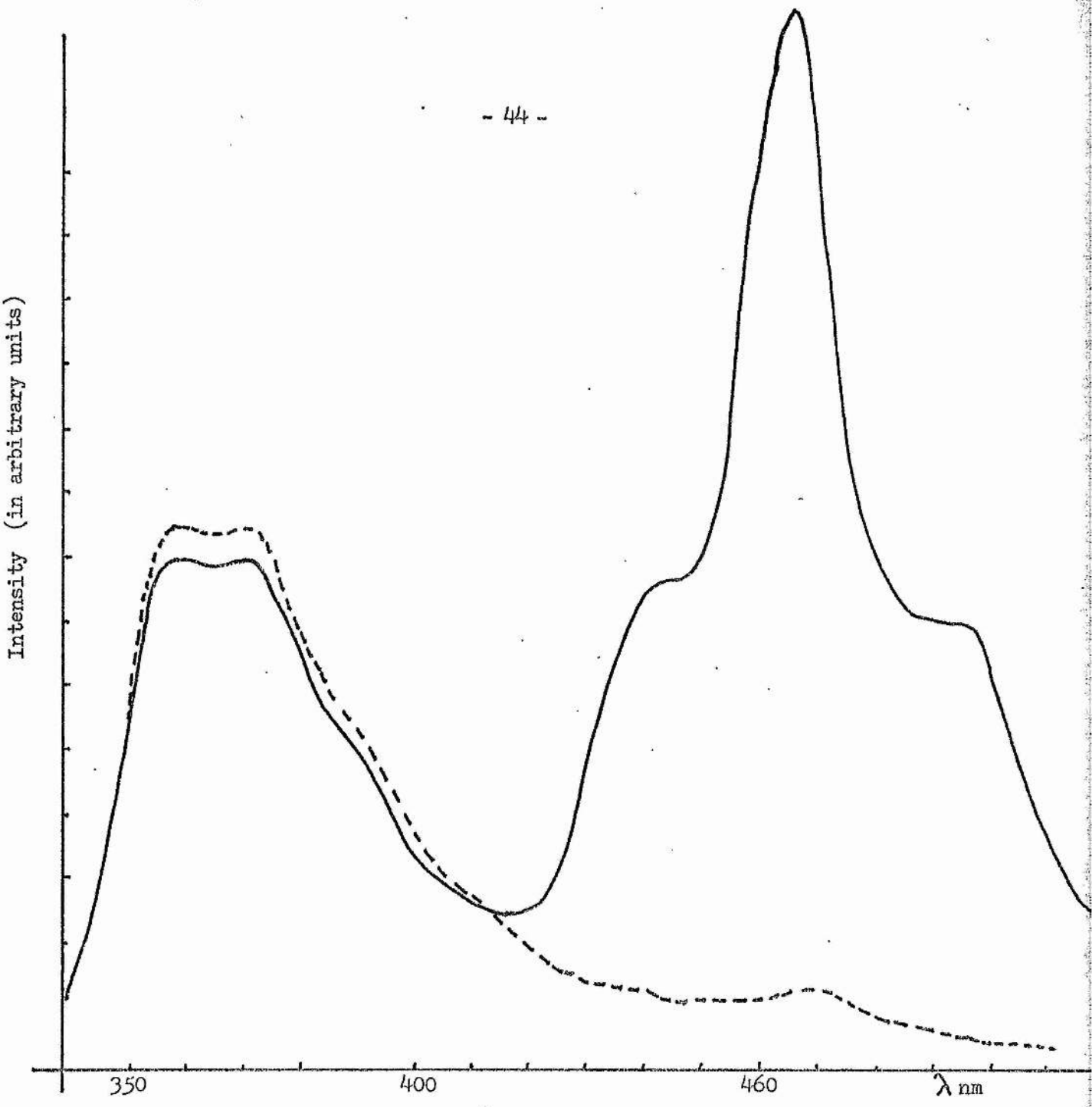


Figure 3.4

Total normalized emission spectra for triphenylene in PMMA, under vacuum (solid line), and under 6.6×10^2 Nm^{-2} of O_2 (broken line).

ii. Curves were obtained when the intensity of fluorescence or phosphorescence, at room temperature, were plotted against intensity of scattered light (Figure 3.5). It is assumed that the intensity of excitation radiation is proportional to the intensity of scattered light.

iii. The decay of triphenylene phosphorescence was found to be exponential at room temperature, even at high intensity of irradiation.

iv. Temperature effect:

The effect of temperature is of great importance since it highlights the interaction between the excited states of the additives and the matrix, and subsequently the mechanism of the different photophysical reactions.

Where a specific system was examined at various temperatures, the Arrhenius equation below was used to calculate the activation energy:

$$k = A \exp^{-E/RT}$$

where A is the pre-exponential factor,

E is the activation energy,

R is the gas constant

T is the absolute temperature.

The intensities of fluorescence and Phos. decay-times were studied over a wide range of temperatures, from room temperature up to 90°C, and the results are shown in figure 3.6 and listed in Table 3.2

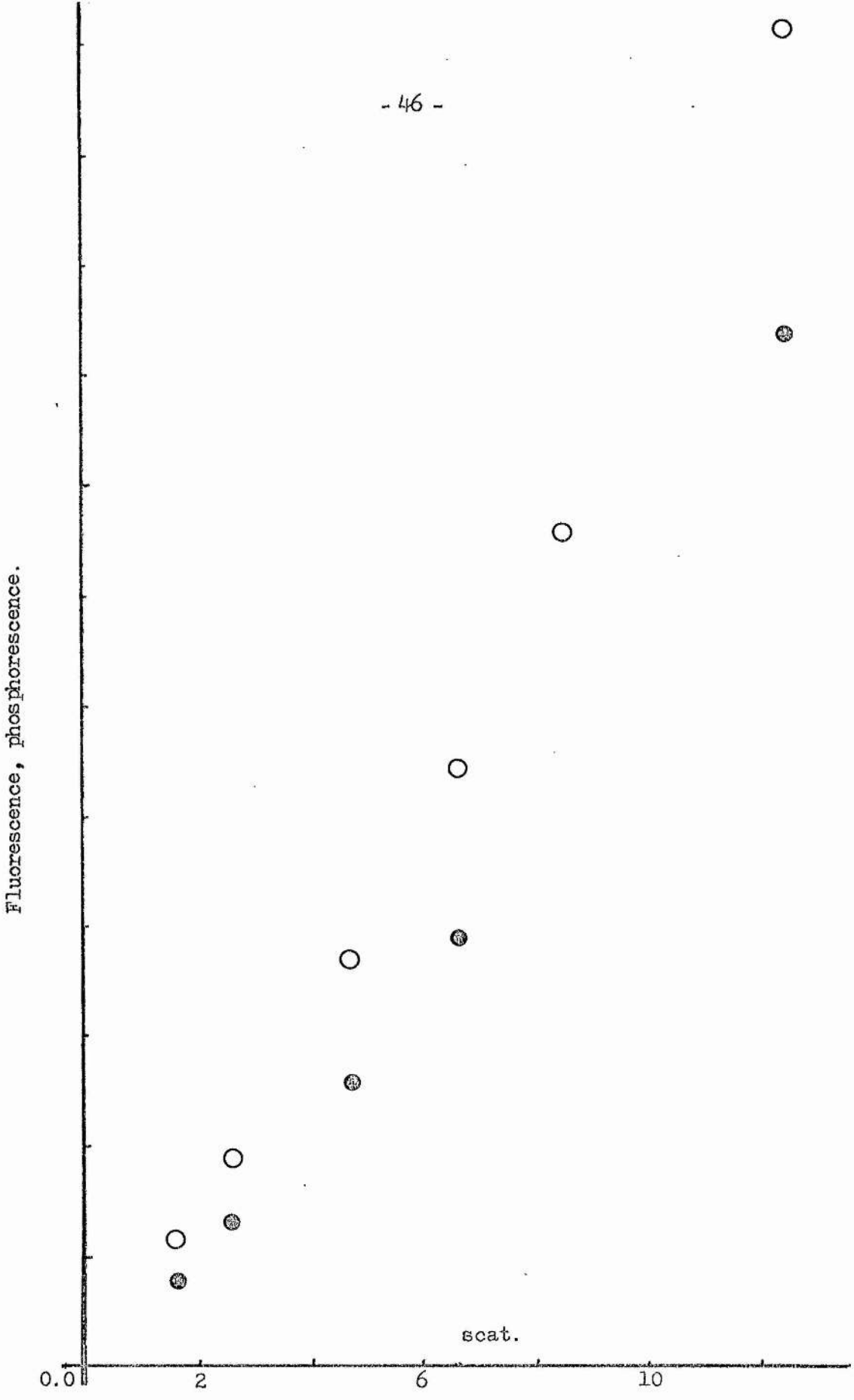


Figure 3.5

Fluorescence (●), and phosphorescence (O) of triphenylene vs. scat. light in PMMA.

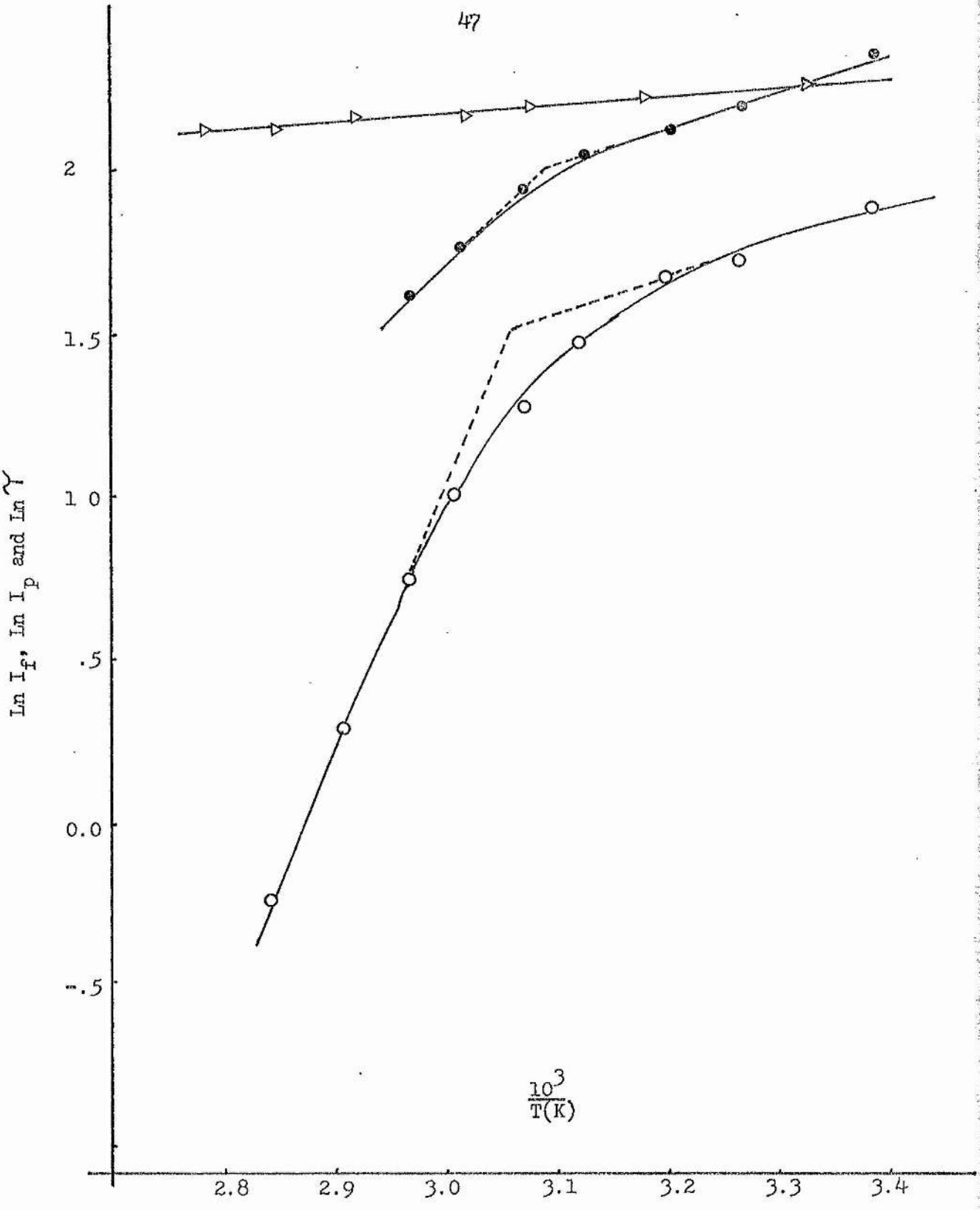


Figure 3.6

Ln intensity of fluorescence, ▷ ; Ln intensity of phosphorescence, o; and Ln γ , ⊙ ; vs. 1/T(K) for triphenylene in PMMA.

TABLE 3.2

Fluorescence, phosphorescence and τ of triphenylene at different temperatures in PMMA. Excitation at 270 nm.

T(°C)	Fluorescence (Arbitrary units)	Phosphorescence (arbitrary units)	τ (sec.)
22.2	5.21	6.54	9.85
33.35	5.02	5.69	8.92
39.55	5.19	5.34	8.42
47.2	5.12	4.4	7.81
52.5	5.03	3.65	6.93
58.9	4.94	2.74	5.92
64.00	4.87	2.12	5.07
71.52	4.78	1.34	2.9
79.1	4.75	0.8	-
89.55	4.69	0.41	-

The fluorescence intensity decreased slightly and gradually with temperature. The activation energy for this process was calculated to be 2.39 kJ $mole^{-1}$. For the phosphorescence decay it is quite clear that a significant deviation from linear behaviour takes place about 52°C (Figure 3.7). Around the same temperature the plot of τ_p vs. 1/T(K) also shows a kink. It is important to keep this point in mind for comparison with results for PVA matrix and discussion later.

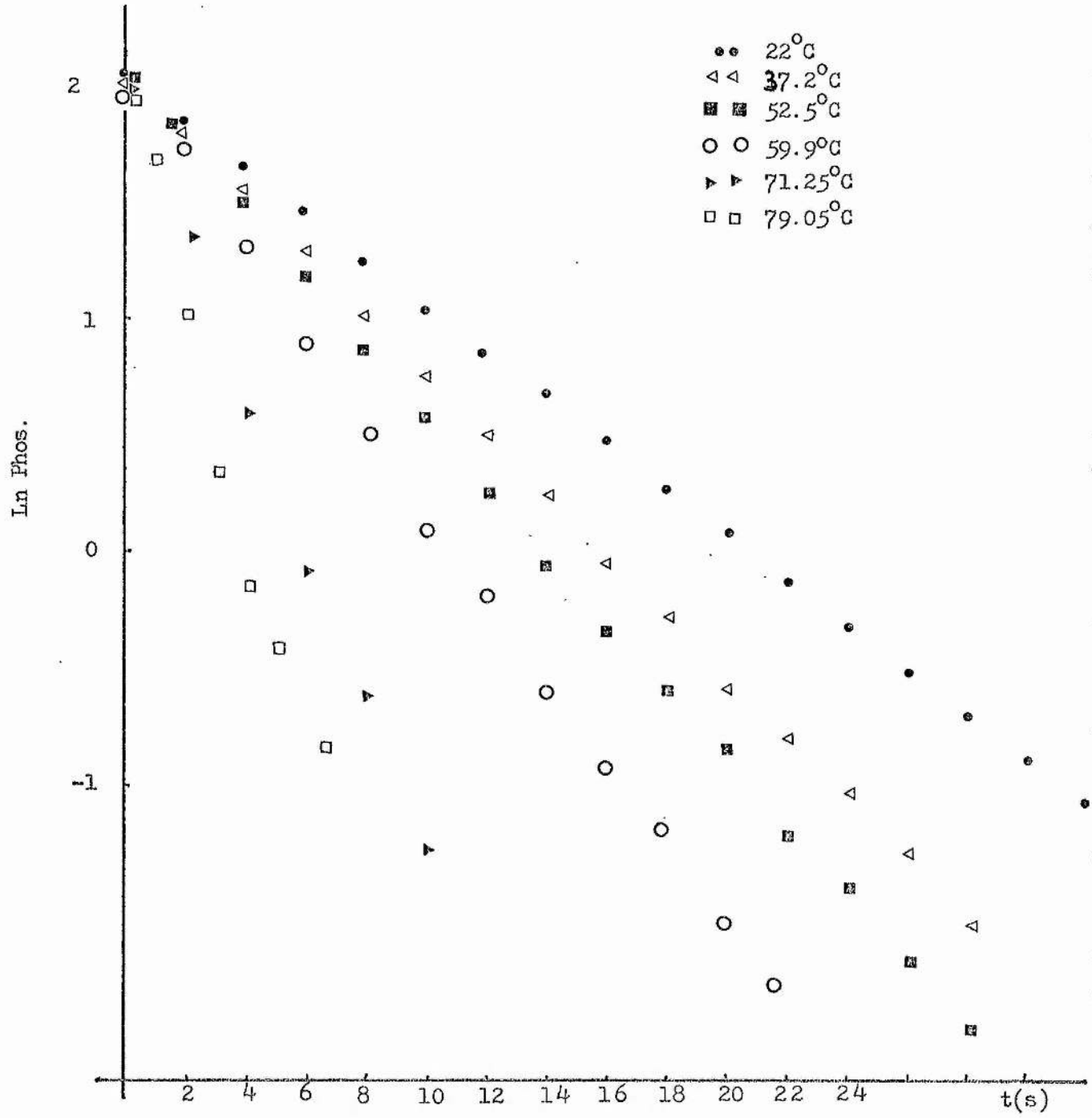


Figure 3.7

Normalized decay of triphenylene phosphorescence in PMMA at different temperatures. Ext/Em. = 270/466 nm.

The activation energy was calculated from the first part of ln. Υ, or ln. phosphorescence, vs. 1/T(K) which represents the exponential behaviour and found to be 10.43 and 11.88 kJ $mole^{-1}$ respectively.

v. Quenching by oxygen

Quenching the electronically excited states of aromatics by low pressure of oxygen, below one atmosphere, is our concern. The apparatus and the procedure have previously been outlined in Chapter 2.

When about 1.33×10^{3} N m^{-2} of O_2 was admitted carefully to the system the phosphorescence intensity decreased. At the same time the fluorescence intensity increased, reaching its maximum value (3.3% more than its original value in vacuum) at 2×10^{3} N m^{-2} of O_2 pressure, then it steadily decreased. Figure 3.8 shows Stern-Volmer (S/V) plot for this quenching process. Variation of fluorescence and phosphorescence intensities with O_2 pressure are collected in Table 3.3

The normal form of the S/V plot requires a knowledge of the concentration of the quencher. In the present case the concentration of O_2 in the polymer film is related to the pressure of gas above the film, thus

$$[O_2] = KP$$

K can be defined as the distribution constant for the polymer and O_2.

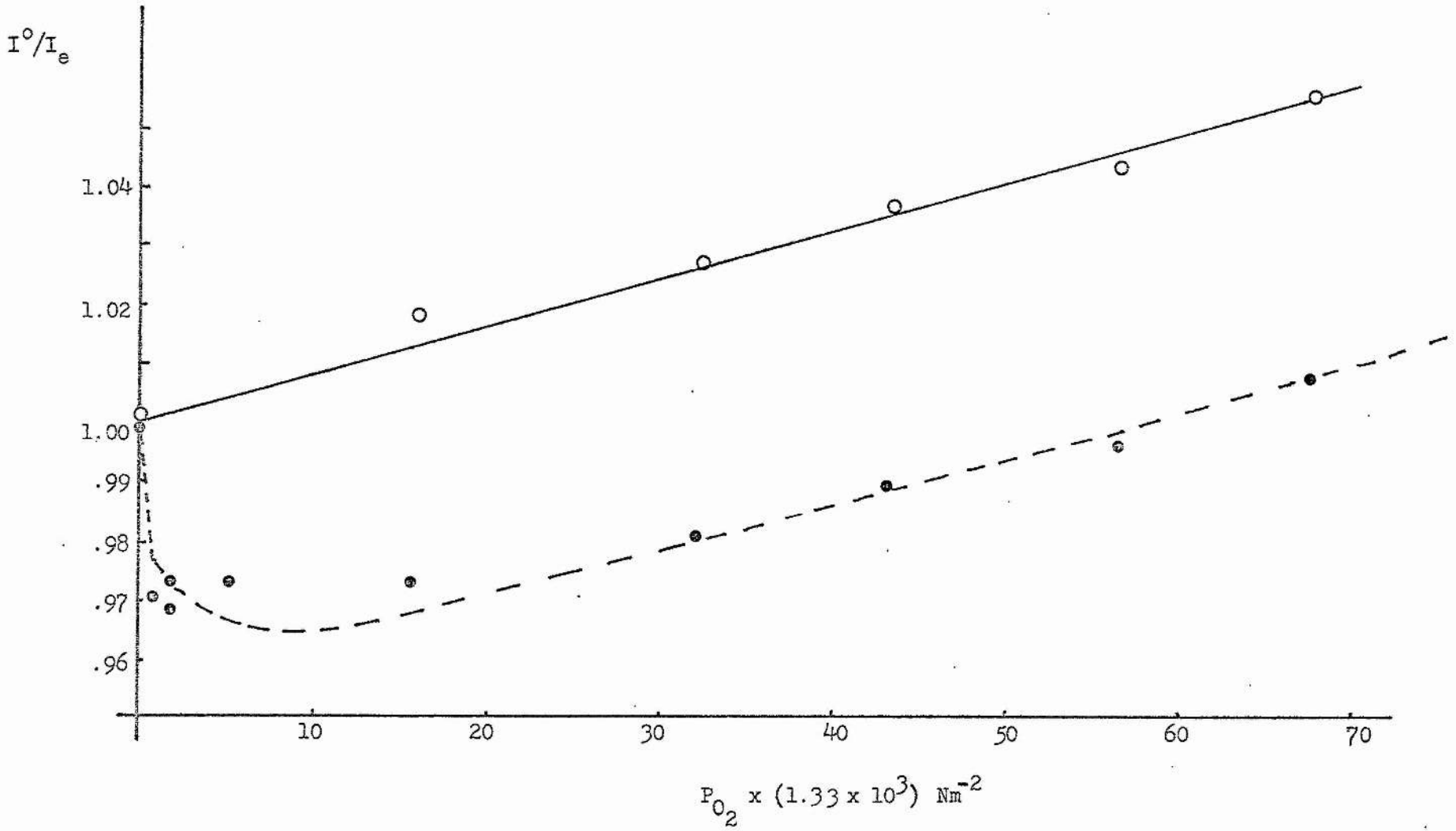


Figure 3.8

The Stern-Volmer plot for the quenching of triphenylene fluorescence by O_2 in PMMA (⊙); and its extrapolated plot (0).

TABLE 3.3

Fluorescence and phosphorescence intensities of triphenylene in PMMA vs. O_2 pressure

P_{O_2} (X 1.33 x 10^3) N m^{-2}	Relative fluorescence intensity	Relative phosphorescence intensity
0.0	4.67	5.63
0.5	4.81	1.09
0.8	4.8	0.33
1.5	4.82	0.01
5.1	4.80	0.0
15.9	4.80	0.0
32	4.76	0.0
43.1	4.72	0.0
56.4	4.69	0.0
67.8	4.63	0.0

The gradient of the straight line from S/V plots enabled the quenching rate constant, k_q, multiplied by the distribution constant, K, to be evaluated. Taking the fluorescence life time, 37[13] ns, to be the same as in liquid state k_q K is found to be 1.3×10 $m^2 N^{-1} s^{-1}$.

When the oxygen was pumped out carefully from the system, the intensity of fluorescence (fluor.) and phosphorescence (phos.) returned to their original values (figure 3.4). The linear part of figure 3.8 was extrapolated and a value of $I_{extr.}$ was obtained. A typical S/V plot was obtained from I_{extr}/I_e against P_{O_2}, including the low values, where I_e is the fluor. intensity at any pressure of O_2, as shown in figure 3.8.

When the sample was left in 9.33×10^2 Nm^{-2} of O_2 for a few hours to remove all triphenylene triplets, a S/V plot of the fluor. intensity vs. P_{O_2} was linear, as shown in figure 3.9 with gradient of 6.75×10^{-7} m^2 N^{-1}.

To highlight the influence of O_2 on the phos. behaviour, our investigations showed that the phos. became non-exponential under O_2. The non-exponentiality increased with increasing O_2 pressure as shown in figure 3.10. The phos. decay time was remarkably reduced to 2.8 sec. under 10^3 Nm^{-2} pressure of O_2.

B. Triphenylene in PEMA and in EMA/MMA copolymer

In (EMA/MMA) 20% and 60% copolymers, I_p/I_f, phos. behaviour and phos. decay time of triphenylene at room temperature (R.T.) and at 77K were found, within experimental error, to be similar to those observed and measured in PMMA matrix, for PEMA τ_p = 8.5 sec. at R.T.

As with our findings in PMMA, the fluor. intensity increased when O_2 gas was admitted and the S/V plot for the quenching of triphenylene fluor. by O_2 in PEMA is shown in figure 3.11 with k_qK of 1.7×10 m^2 N^{-1} s^{-1}.

In an attempt to probe the effect of the concentration of the additives on photophysical behaviour, the concentration of triphenylene in (EMA/MMA) 60% was increased to 10^{-1}M. The decay

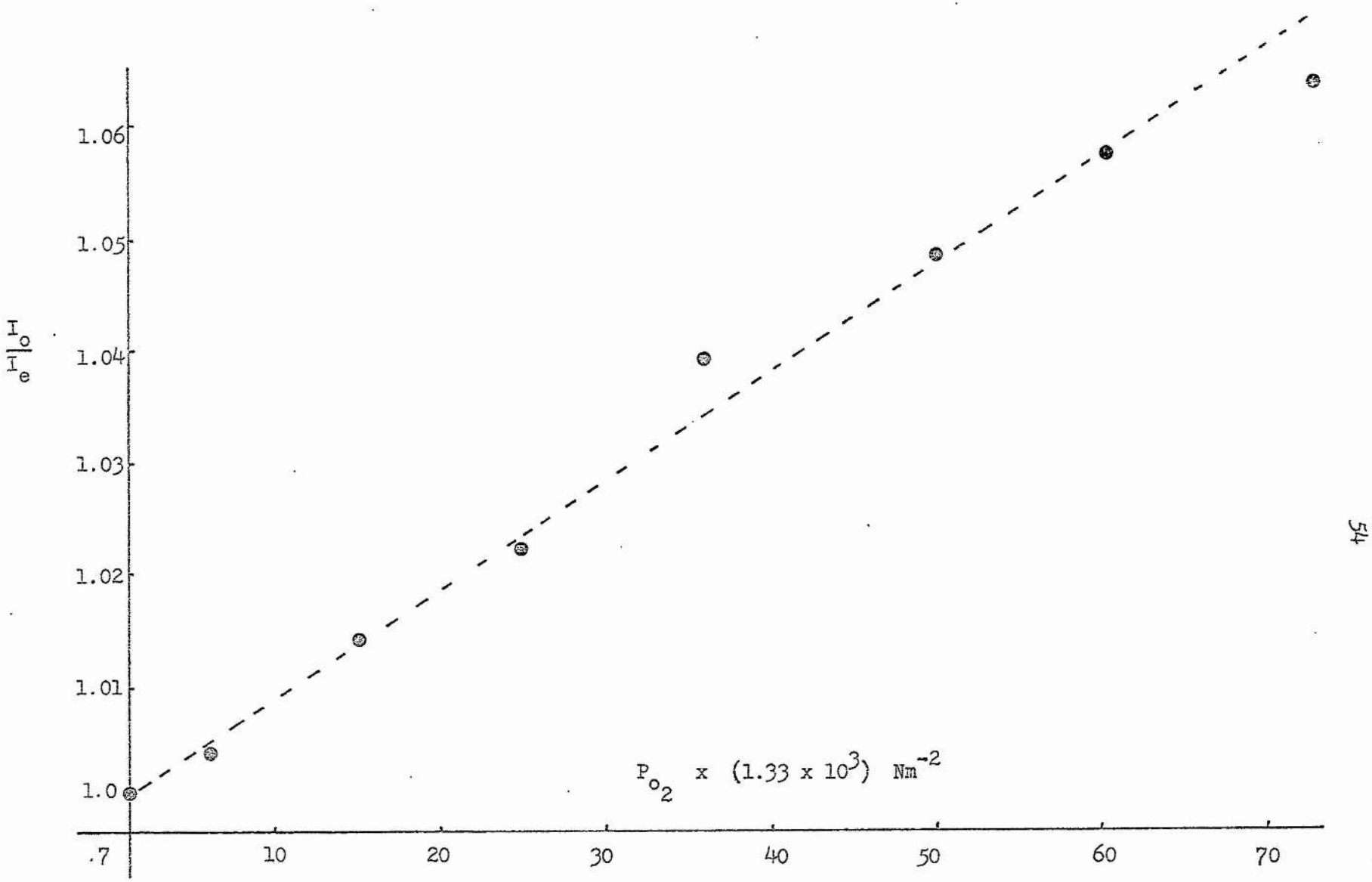


Figure 3.9

Stern-Volmer plot for quenching the fluorescence of triphenylene by O_2 in PMMA. after the sample had been left with low pressure of O_2.

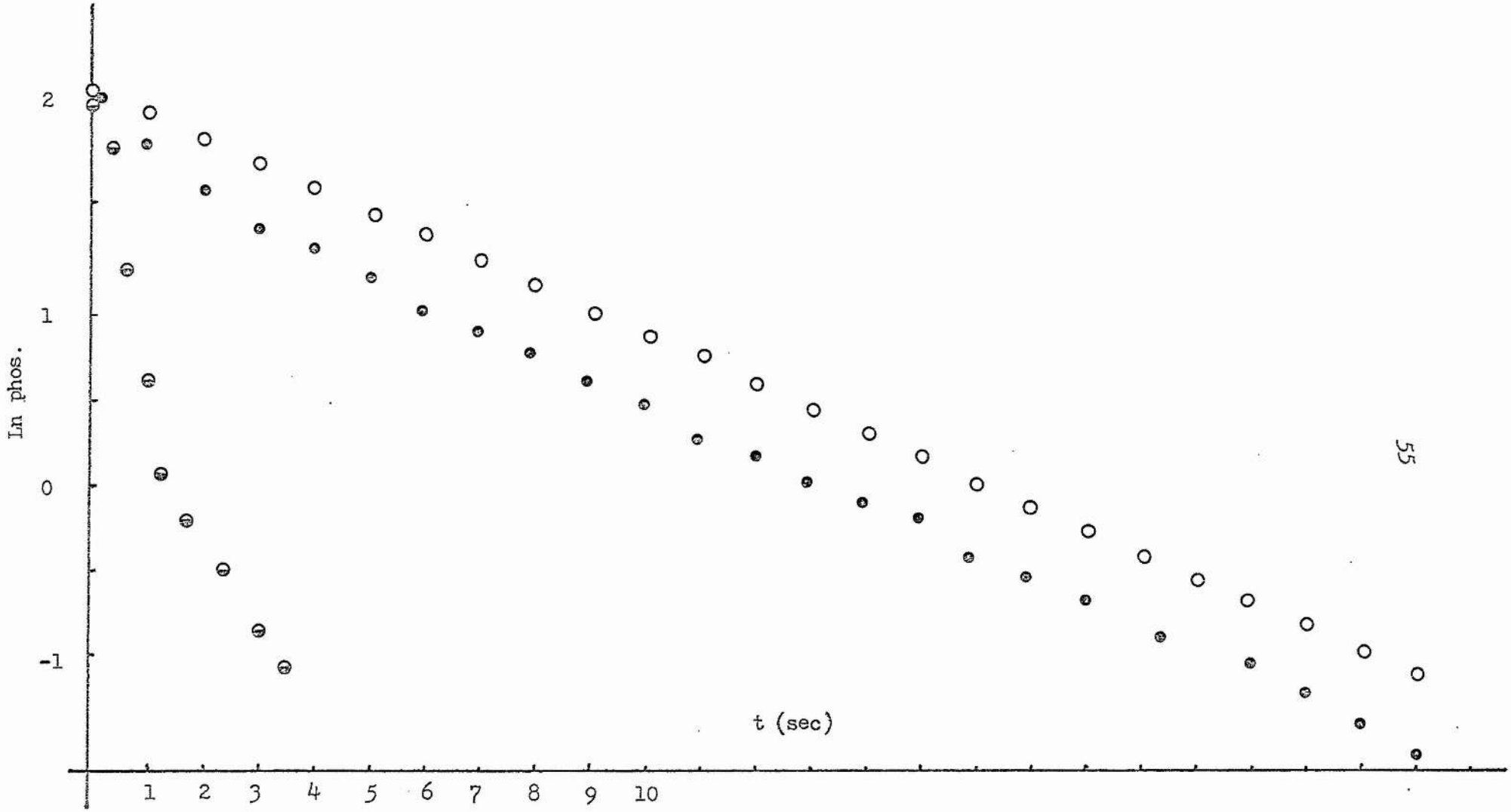


Figure 3.10

Normalised phosphorescence decay of triphenylene in PMMA, in vacuum (O); under 6.66×10^{-2} Nm^{-2} of O_2 (⊕) and under 10^3 Nm^{-2} of O_2 (⊖). Ext/Em = 270/466 nm.

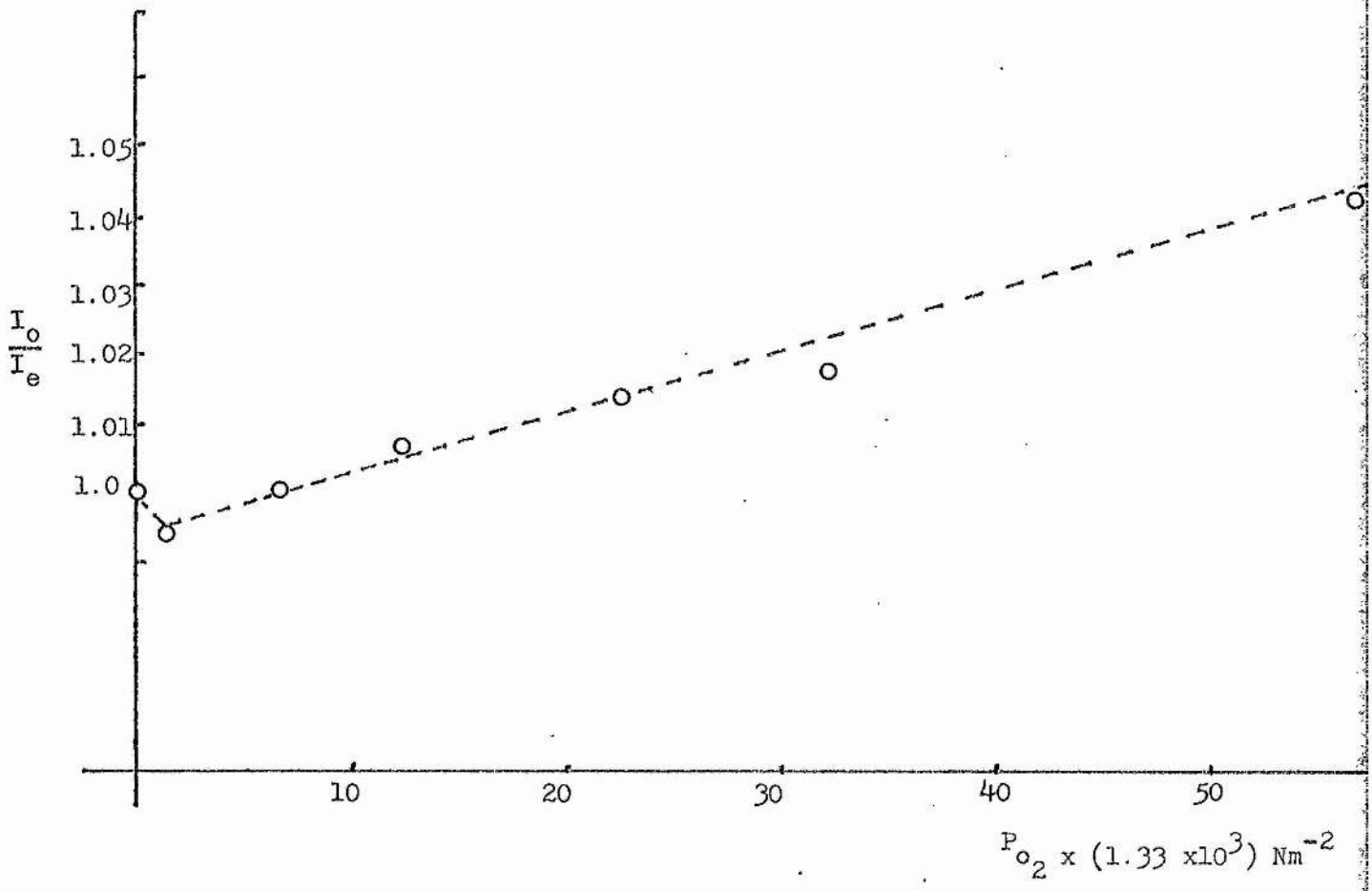


Figure 3.11

Stern-Volmer plot for the quenching of triphenylene fluorescence by O_2 in PEMA. Ext/Em = 270/355 nm.

of phos. was found to be non-exponential, and it was interesting to find that the ratio I_p/I_f was constant at different intensities of irradiation light. The phos. lifetime for triphenylene was measured in this sample and found to be 8.76 and 13.7 sec. at R.T. and at 77K respectively. A similar form of S/V to that observed in PMMA was obtained when the fluorescence of the additive was quenched by O_2, k_qK was measured as 9.33×10 $m^2 N^{-1} s^{-1}$.

C. Triphenylene in PVA

PVA has a T_g at 30^oC[122], so it provides the opportunity to study the behaviour of additives in a rubber-like state at R.T.

In this matrix at R.T. the phos. intensity of triphenylene exceeded that of fluor. A plot of decay of phos. versus time for a wide range of temperatute is shown in figure 3.12 and decay time values are listed in Table 3.4.

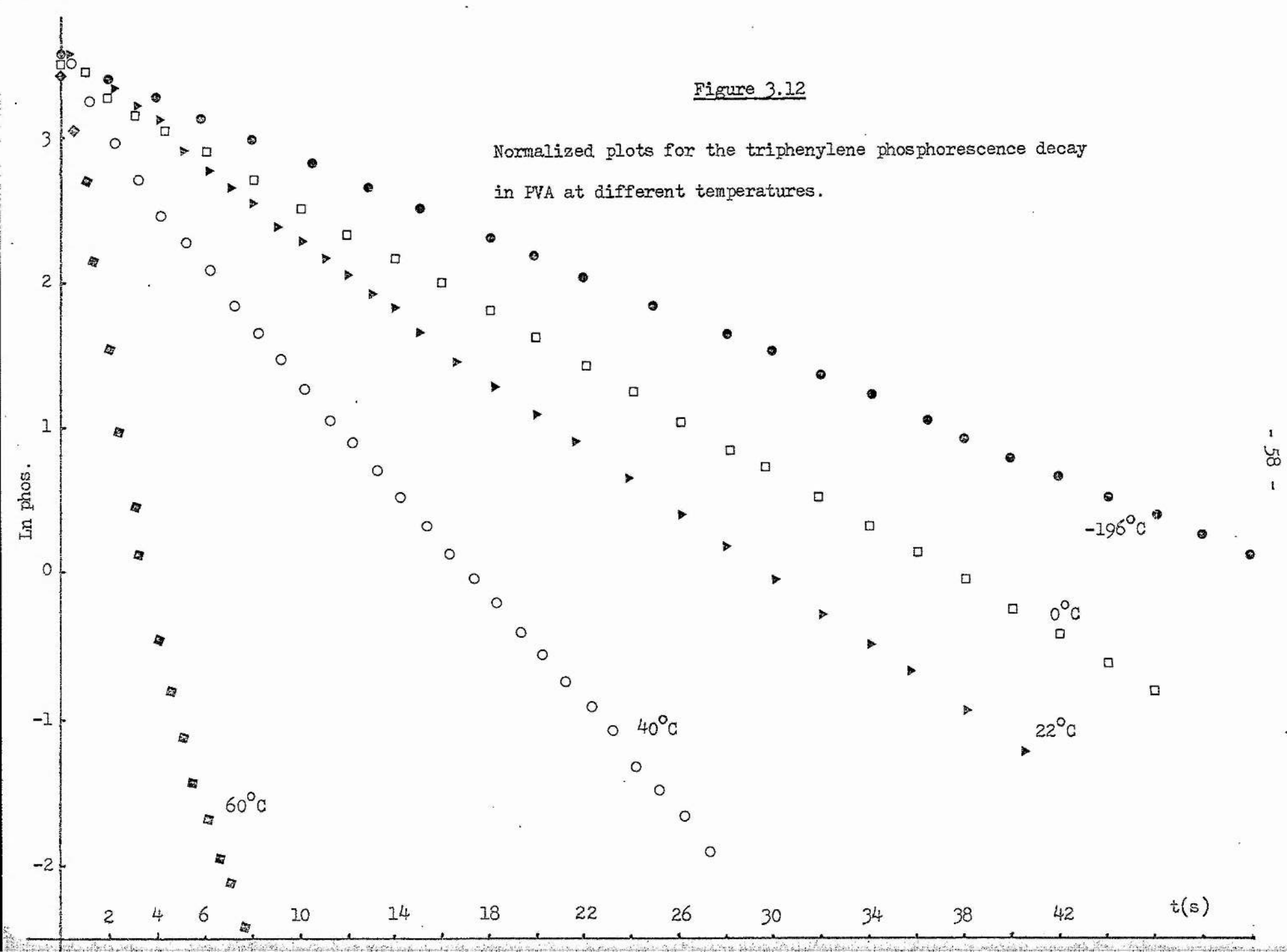
TABLE 3.4

Phosphorescence lifetime of triphenylene in PVA at different temperatures.

T(^oC)	τ (sec.)
-196	14.4
0	10.69
22	8.57
40	6.05
60	1.9

Figure 3.12

Normalized plots for the triphenylene phosphorescence decay in PVA at different temperatures.



It is clear from figure 3.12 that the phos. decay is non-exponential at R.T. ($22^{\circ}C$). The extent of non-exponentiality did not increase significantly at $40^{\circ}C$ (above T_g). Figure 3.13 presents the plot of ln. τ against 1/T(K) of triphenylene in PVA along with that in PMMA for purpose of comparison and discussion later. The plot does not conform to Arrhenius form, since a "bend" occurs at $36.5^{\circ}C$. The activation energy for the lower temperature part of the plot was found to be 7.87 kJ mol^{-1}. (Value for PMMA is 10.43 kJ mol^{-1}).

D. Triphenylene in Pst, pαmst and in (St-αmst) block copolymer

Polystyrene, poly(α-methylstyrene), P α mst, and (st- α mst) block copolymer provide matrices of a different nature from those previously investigated. In particular they cover a wide range of T_g from approximately $100^{\circ}C$ for Pst up to $200^{\circ}C$ for P α mst.

Great care was taken to remove all oxygen from the system by pumping out under high vacuum for a long time before making any measurements.

We have observed that the phos. of triphenylene in these polymers relative to fluor. is very weak at R.T. even when they are excited at 310 nm. where the polymers do not absorb radiation. At 77K the phos. was observed to be very intense with $I_p/I_f > 2$, and this ratio did not vary with changing wavelength of excitation. The values of triphenylene phos. lifetime obtained in these polymers are included in Table 3.5.

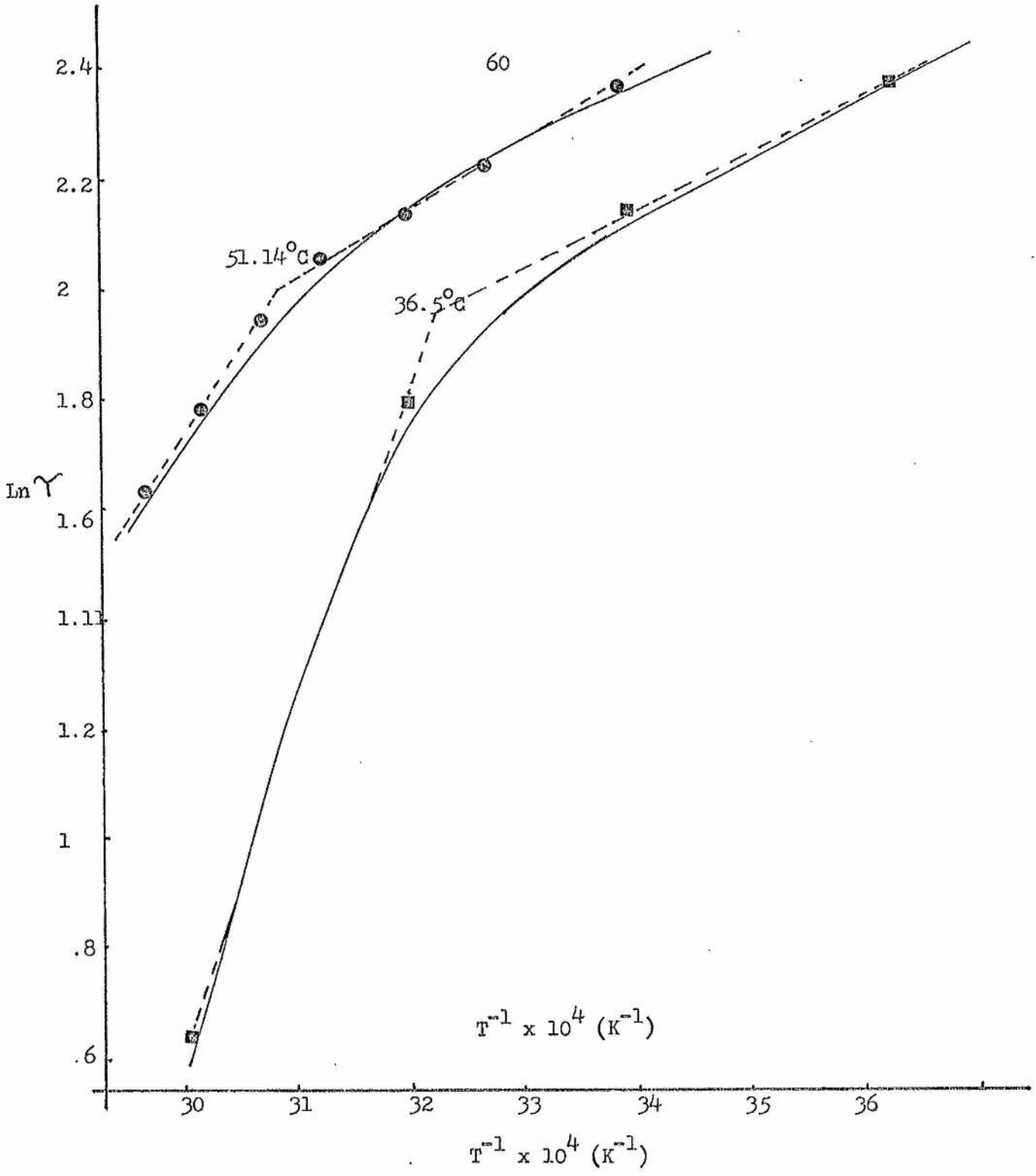


Figure 3.13

Plots of Ln ϒ vs. reciprocal temperature for triphenylene in PMMA (●) and in PVA (■).

TABLE 3.5

τ of triphenylene in Pαmst, Pst and in their block copolymer

Polymer	τ (sec.) R.T.	0°C	77K
Poly(α-methylstyrene)	4	5.1	12.7
(St-αmst) block copolymer	3.73	3.29	11.7
Pst	3.5	-	11.9

The decay of phos. was observed to be non-exponential at R.T. in the above matrices as shown in figures 3.14 and 3.15.

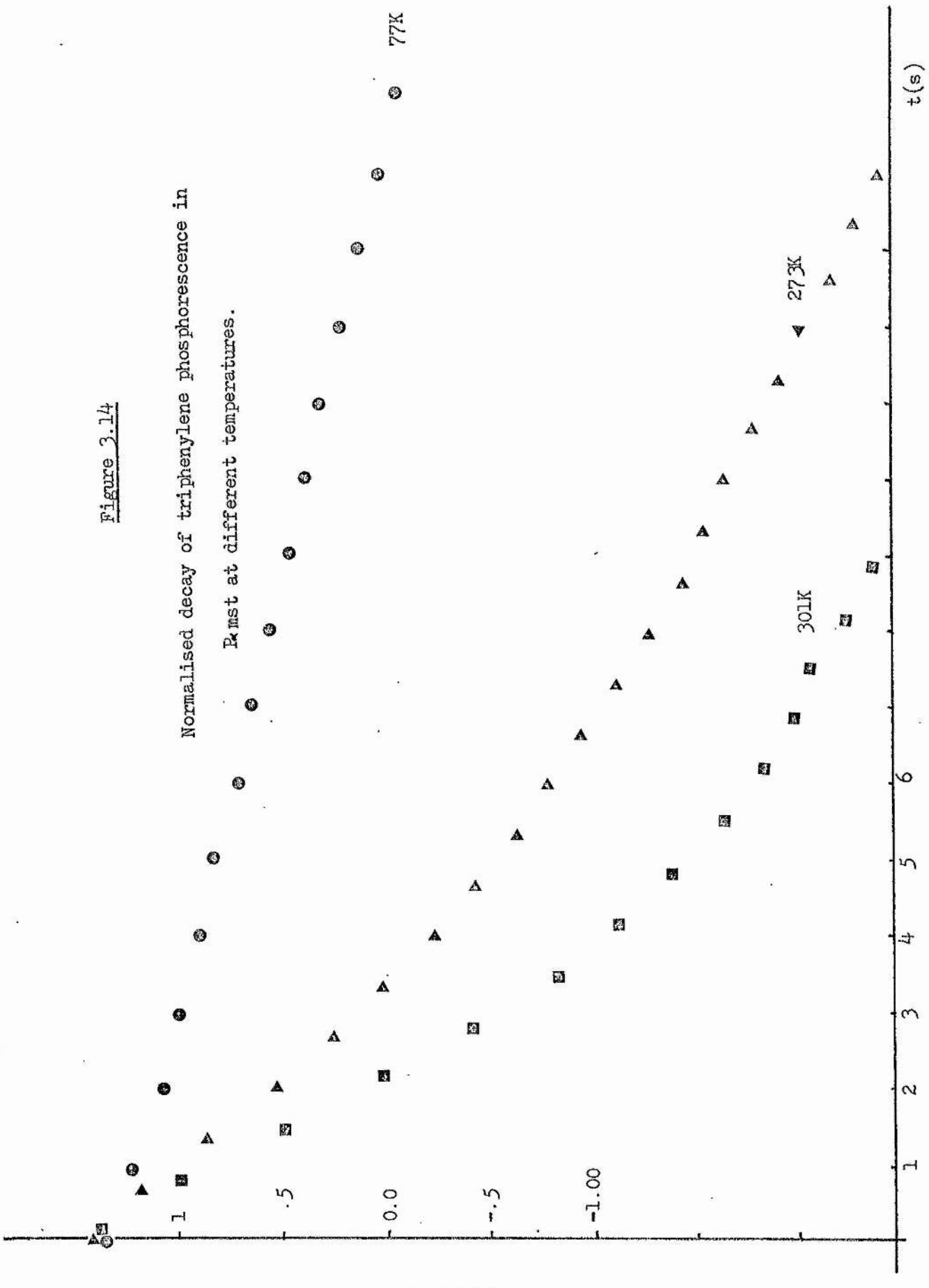
Stern/Volmer plots for quenching of triphenylene fluor. by O_2 in Pst and (St-αmst) block copolymer are shown in figure 3.16 and 3.17. Figure 3.18 illustrates the I_p/I_f ratio at different temperatures in Pαmst. In the same matrix, the plot of ln. intensity of phos. versus 1/T(K) was found to be linear with $\Delta E = 11.78$ kJ mol^{-1} as presented in figure 3.19.

E. Triphenylene in (St-MMA) copolymers

Investigation of the behaviour of aromatics in (St-MMA) copolymers emphasises the influence of the phenyl group on their phos. behaviour. Experiments of this nature have been made and phosphorescence lifetime of triphenylene in different St-MMA

Figure 3.14

Normalised decay of triphenylene phosphorescence in Rmst at different temperatures.



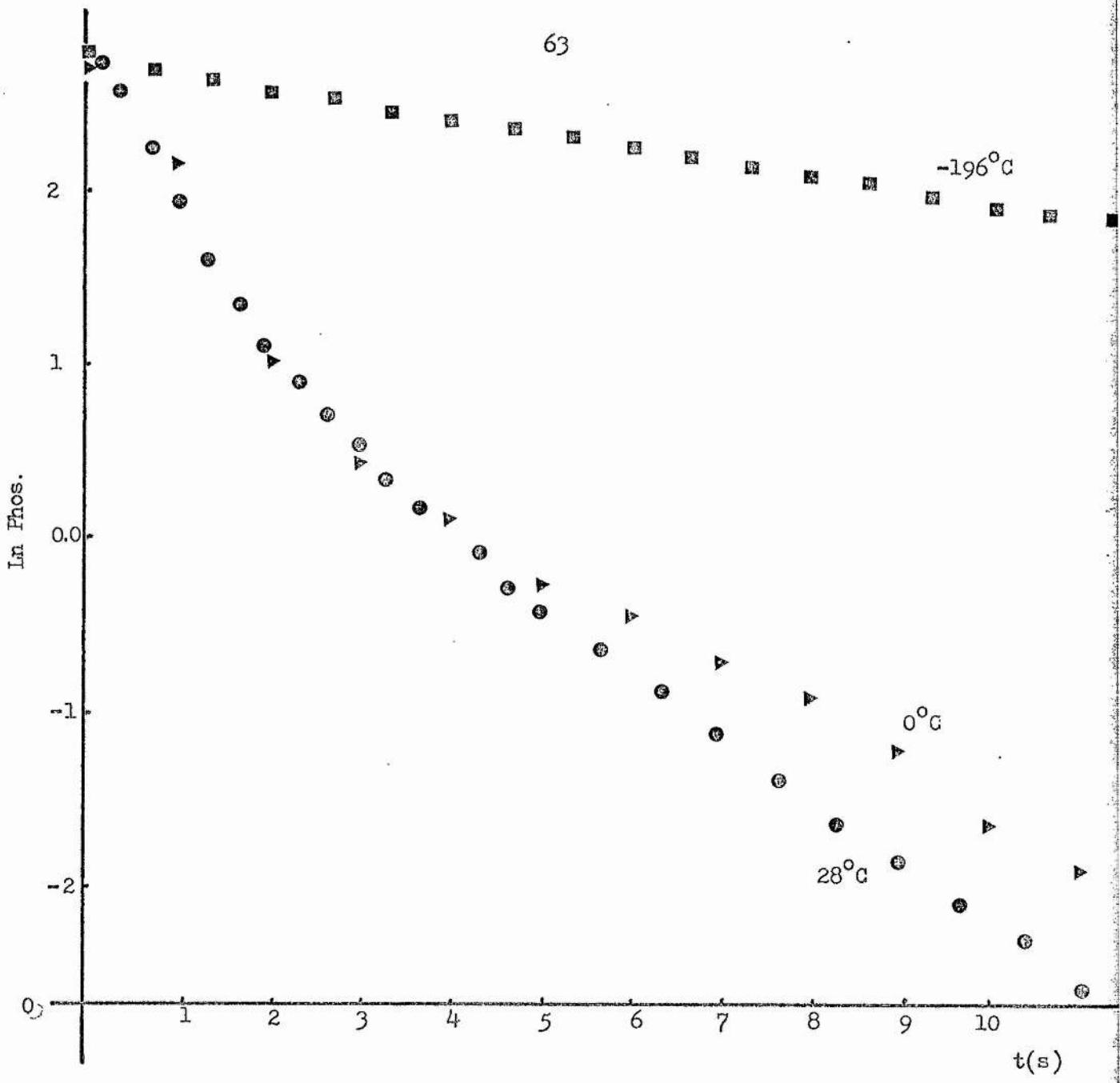


Figure 3.15

Normalized decay of triphenylene phos. in Poly(St-∝mst) block co-polymer, in vacuum and at different temperatures.

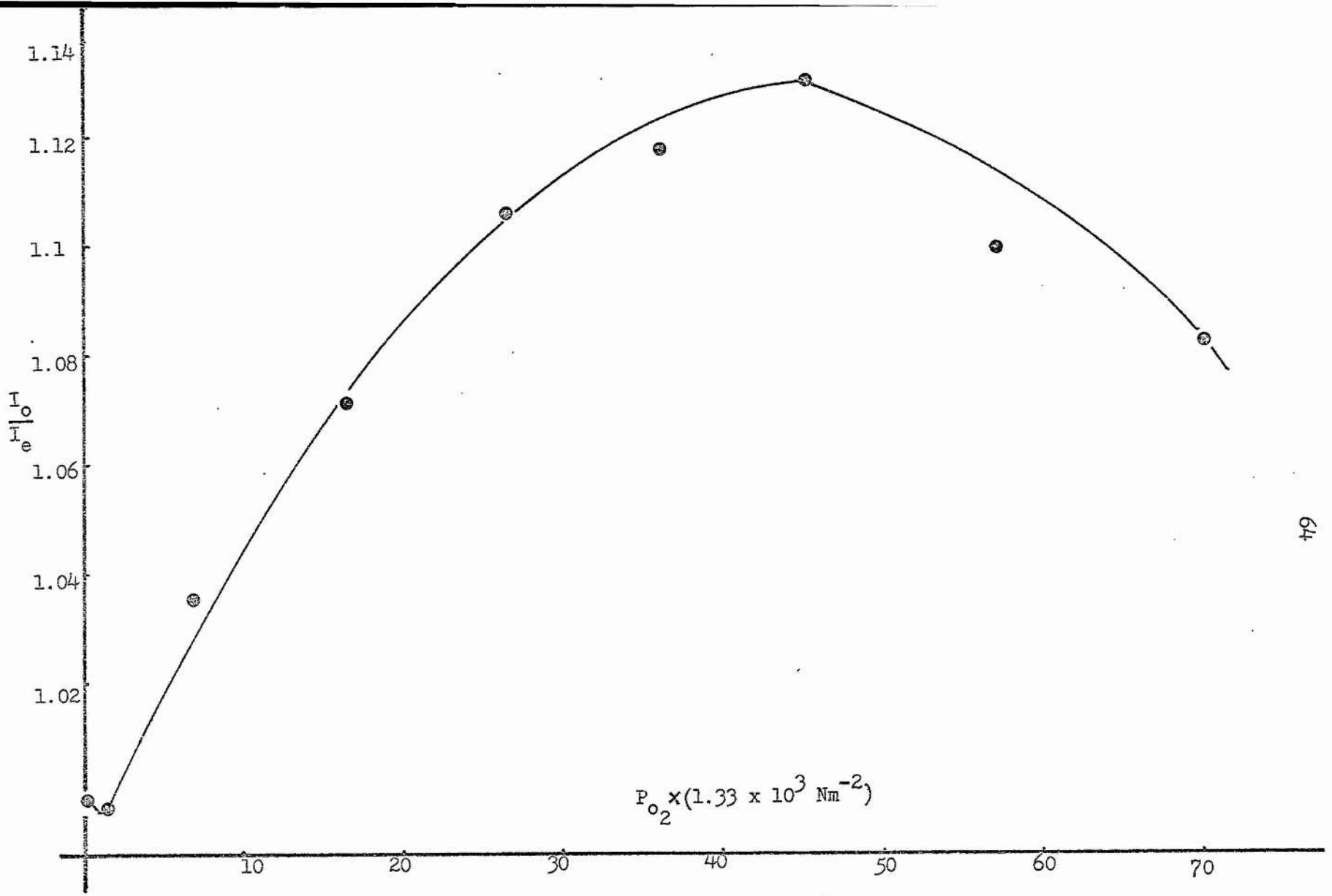


Figure 3.16

S/V plot for quenching Tri. fluorescence by O_2 in Pst. Ext/Em = 290/356 nm.

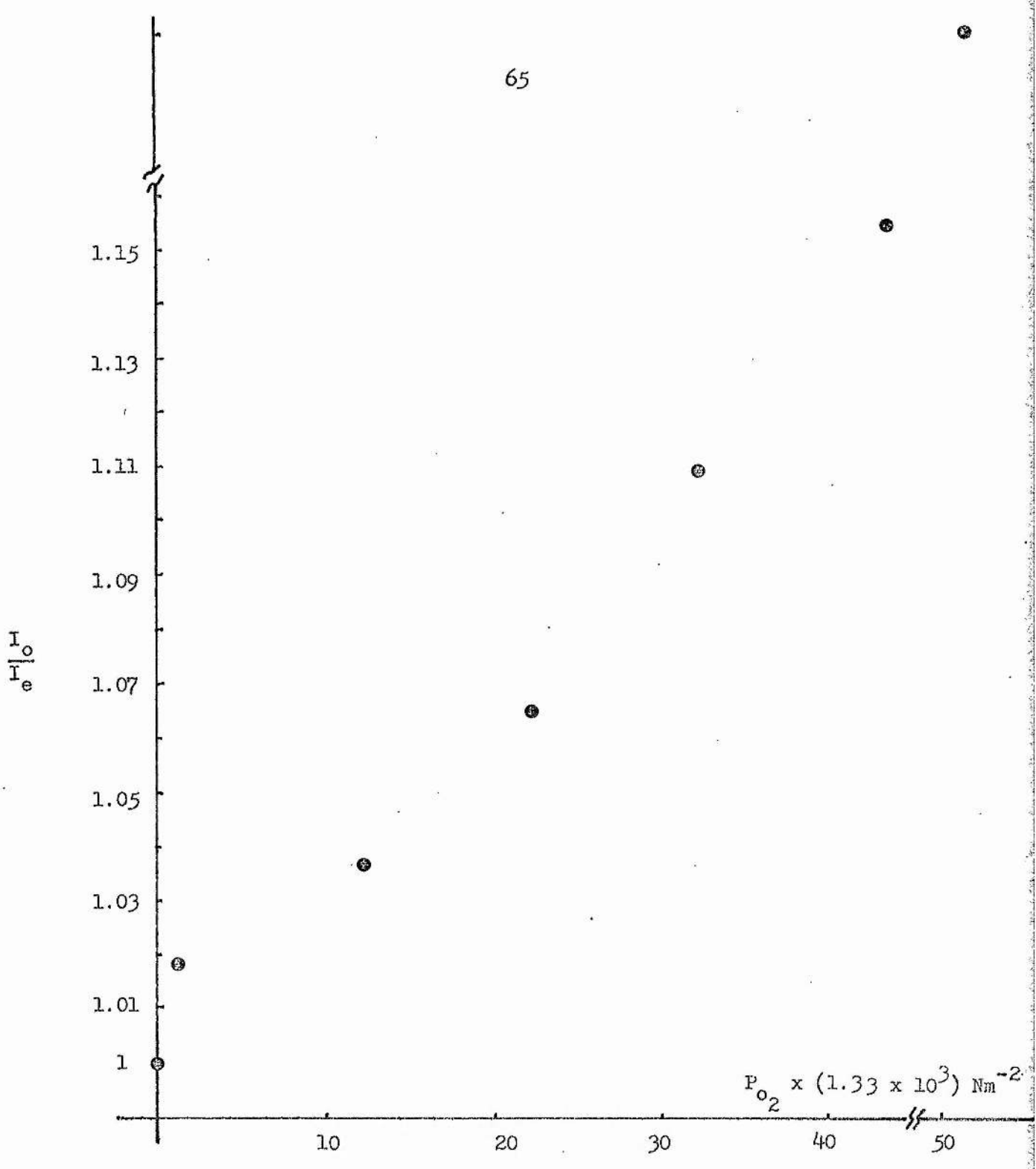


Figure 3.17

Stern-Volmer plot for the quenching of triphenylene fluorescence in (St-αmst) block co-polymer by O_2.
Ext/Em = 270/356 nm.

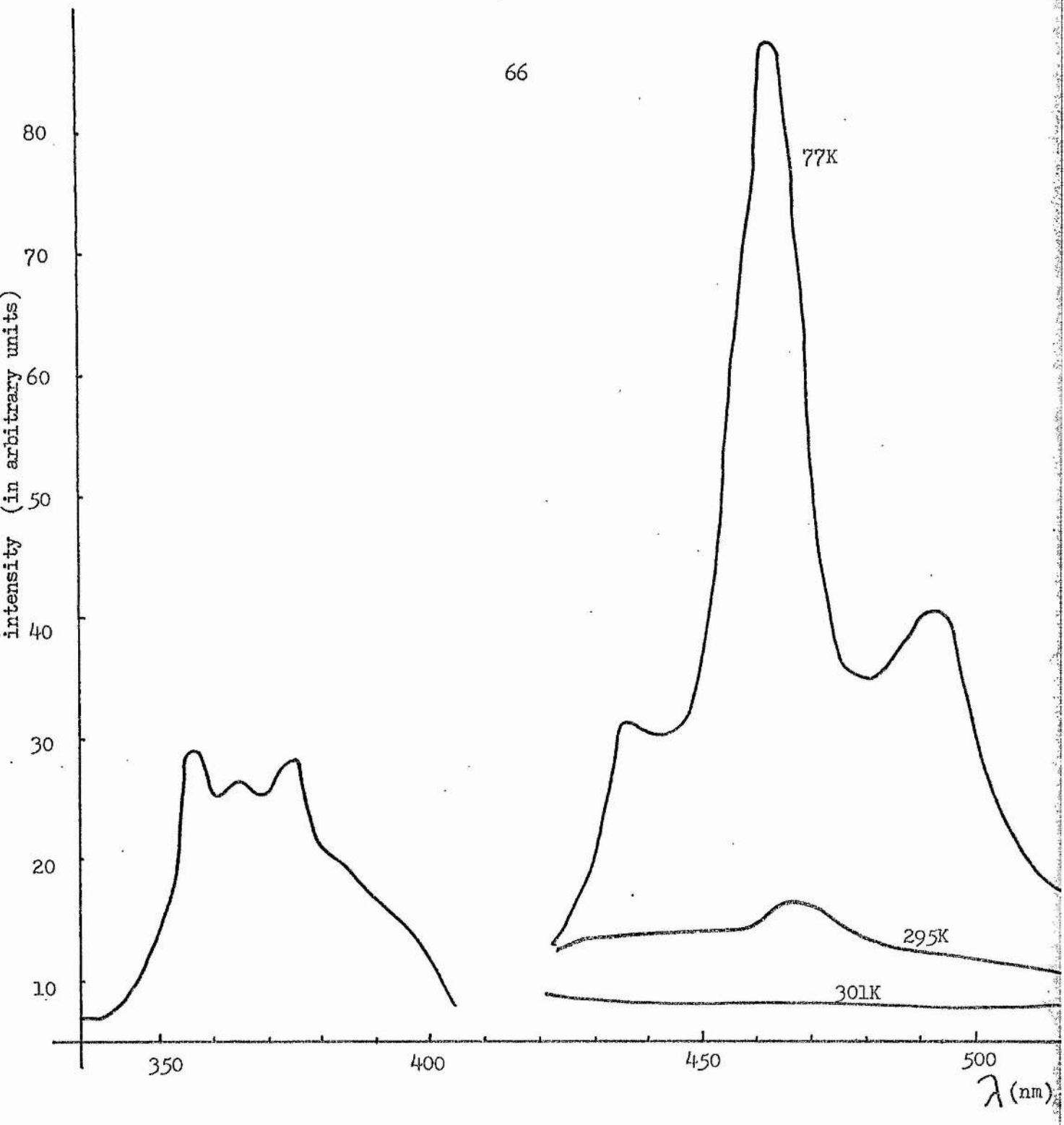


Figure 3.18

Phosphorescence relative to fluorescence of triphenylene in Perspex at different temperatures. Excitation at 300 nm.

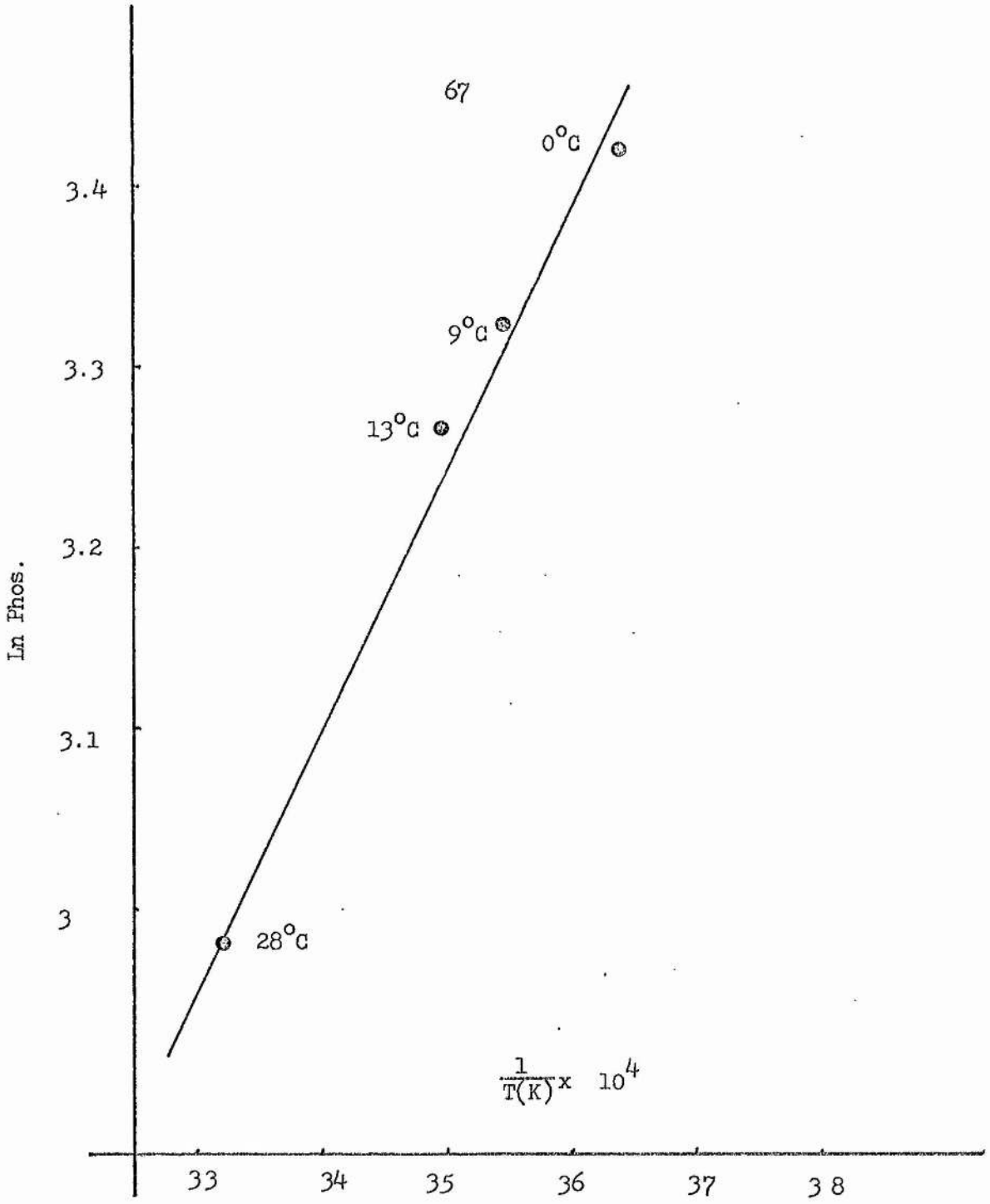


Figure 3.19

Ln phosphorescence vs. reciprocal temperature for triphenylene in P∝mst.

copolymers at R.T. and at 77K are listed in Table 3.6.

TABLE 3.6

Phosphorescence decay time of triphenylene in (St-MMA) copolymers

Mole fraction of styrene unit	R.T. τ (sec.)	R.T. $^{o}\tau/^{s}\tau$	77K τ (sec.)	77K $^{o}\tau/^{s}\tau$
0.0 (PMMA)	9.8[a]	1	15.1[b]	1
0.05	9.7	1.0103	14.85	1.0168
0.187	7.65	1.281	13.57	1.1127
0.58	6.419	1.526	12.46	1.211
0.78	4.47	2.192	12.0	1.258
1.00 (Pst)	3.5	2.8	11.9[c]	1.268

lit. values
a - 9.4 sec. from ref. 33
b - 15 sec. from ref. 137
c - 11.5 sec. from ref. 137

A Stern/Volmer type of treatment for the lifetime of triphenylene phos. against mole fraction of styrene unit revealed a linear plot as shown in figure 3.20. The slope was measured and k_q evaluated at 77K (values and mechanism will be discussed in a

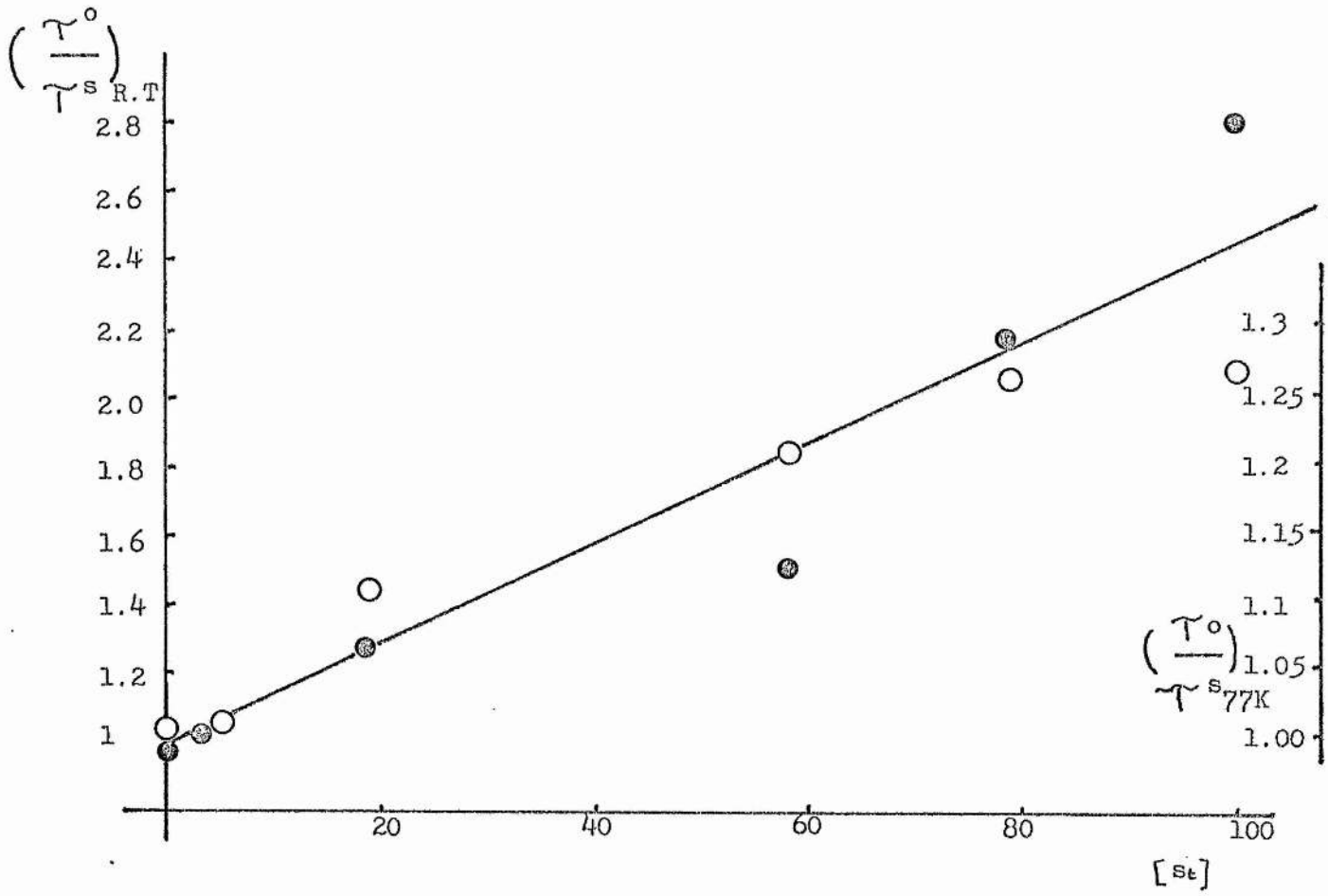


Figure 3.20

Stern-Volmer plots for the quenching of phosphorescence life time of triphenylene by styrene unit in (St-MMA) co-polymers at 77K (O) and at R.T. (●).

later chapter). Finally, the phosphorescence decay of triphenylene in these copolymers are shown in figure 3.21

2. Coronene

Figure 3.22, 3.23 and 3.24 show that coronene absorbs and emits light in a region of the spectrum removed from those of the polymers used as a matrices.

In vacuum and with PMMA matrix, excitation at 306 nm results in reaching a maximum value for intensity of coronene fluor. at 448 nm in 2 sec. A decay in the intensity follows till a steady state value is achieved after 21 sec. Simultaneously, the phos. intensity increased continuously to a steady value in the same time, 21 sec. Under oxygen the fluorescence intensity did not decay after it had reached its maximum value (figure 3.25). This "overshoot" behaviour was found to occur in different plastic media like Pst and its copolymers with PMMA, PVA and in PMMA when DABCO or cyasorb 1084 are present, at R.T. or at 77K.

The plots of fluorescence (the maximum value) and phos. of coronene against intensity of scattered light in different plastic media were found to be straight lines, passing through the origin with different slopes (figure 3.26), whereas a curve was obtained when the steady state of fluor. was plotted against intensity of scattered light. I_f/I_p ratio may be obtained by dividing the slope of fluor. versus scattering light by that for phos. versus scattered light.

Typical exponential behaviour for phos. decay time of coronene in different plastic media have been observed at R.T. and even at very high intensity of exciting light. Table 3.7 lists τ_p of coronene under different conditions.

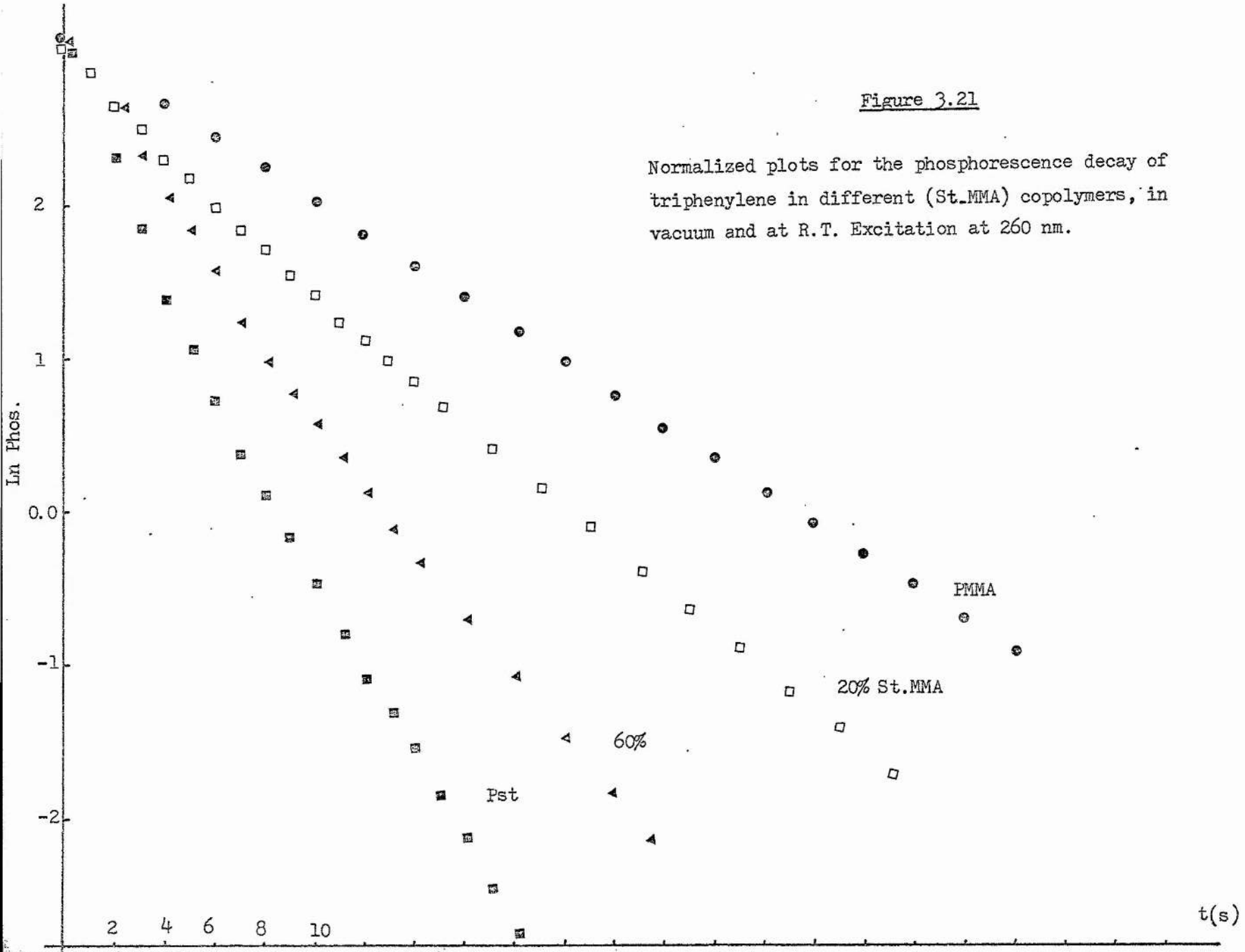


Figure 3.21

Normalized plots for the phosphorescence decay of triphenylene in different (St.MMA) copolymers, in vacuum and at R.T. Excitation at 260 nm.

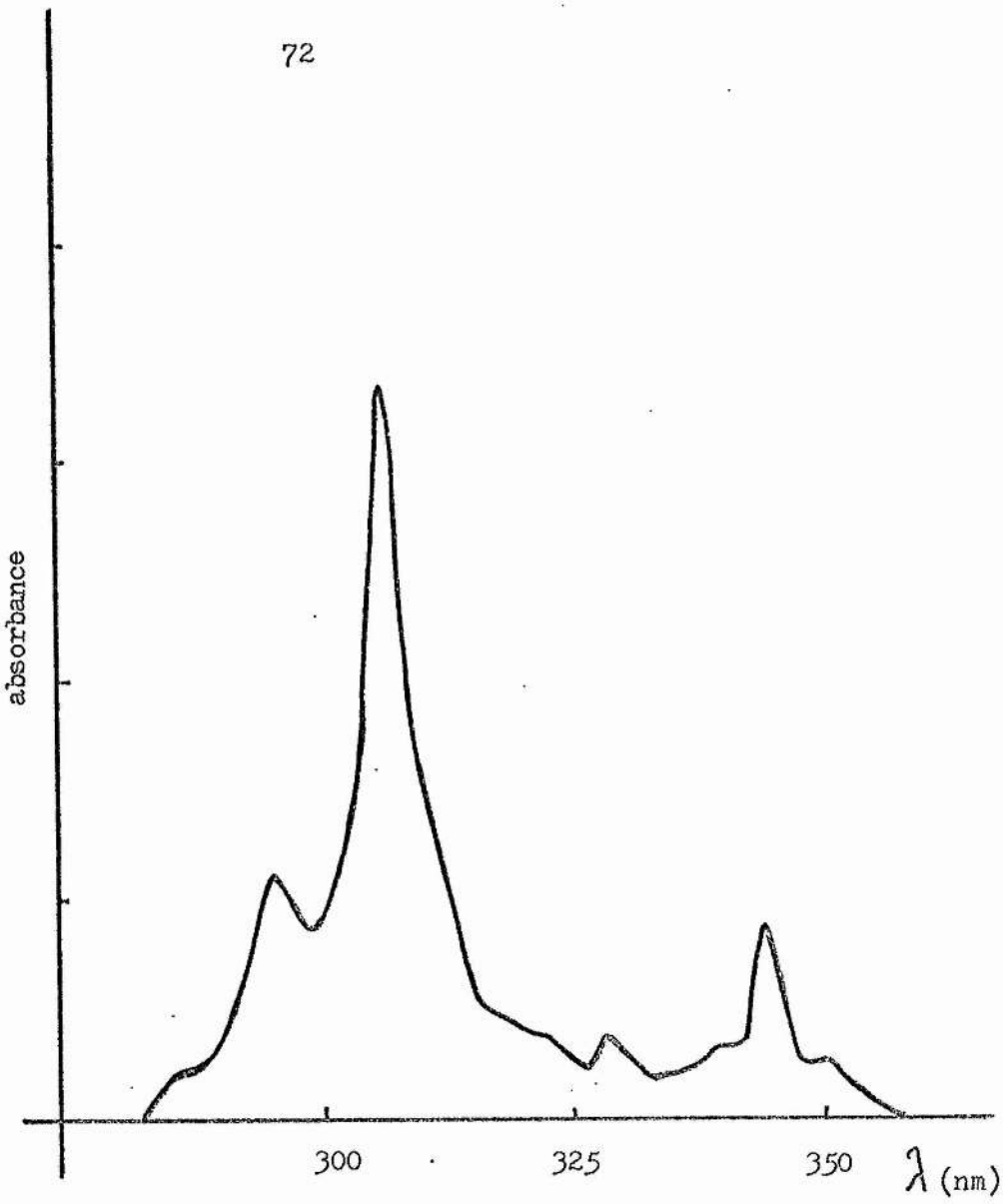


Figure 3.22

Absorption spectrum of coronene in benzene.

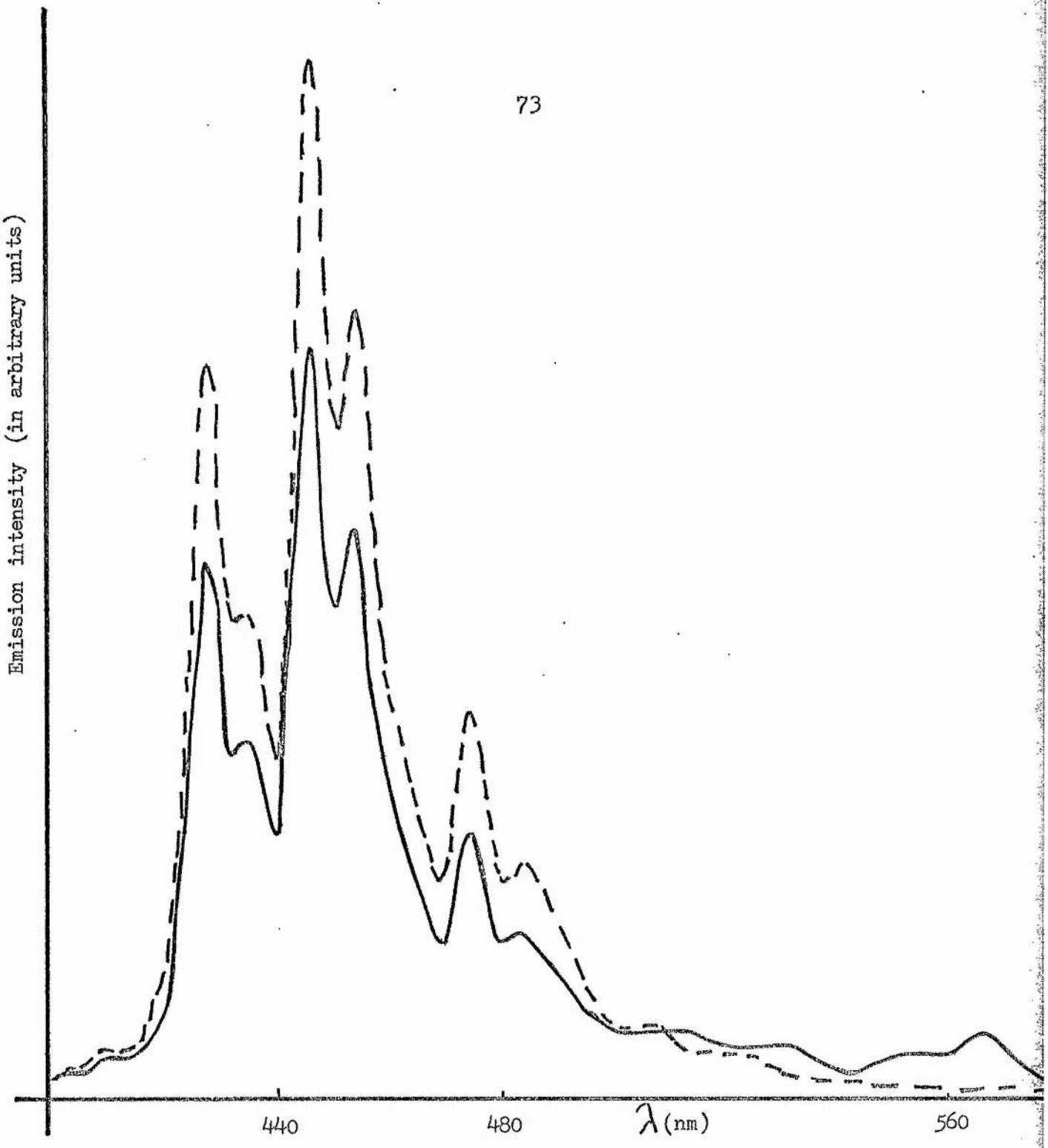


Figure 3.23

Total emission spectrum of coronene in PMMA, under vacuum (solid line), and under low pressure of O_2 (broken line) and at the same conditions. Excitation wavelength 306 nm.

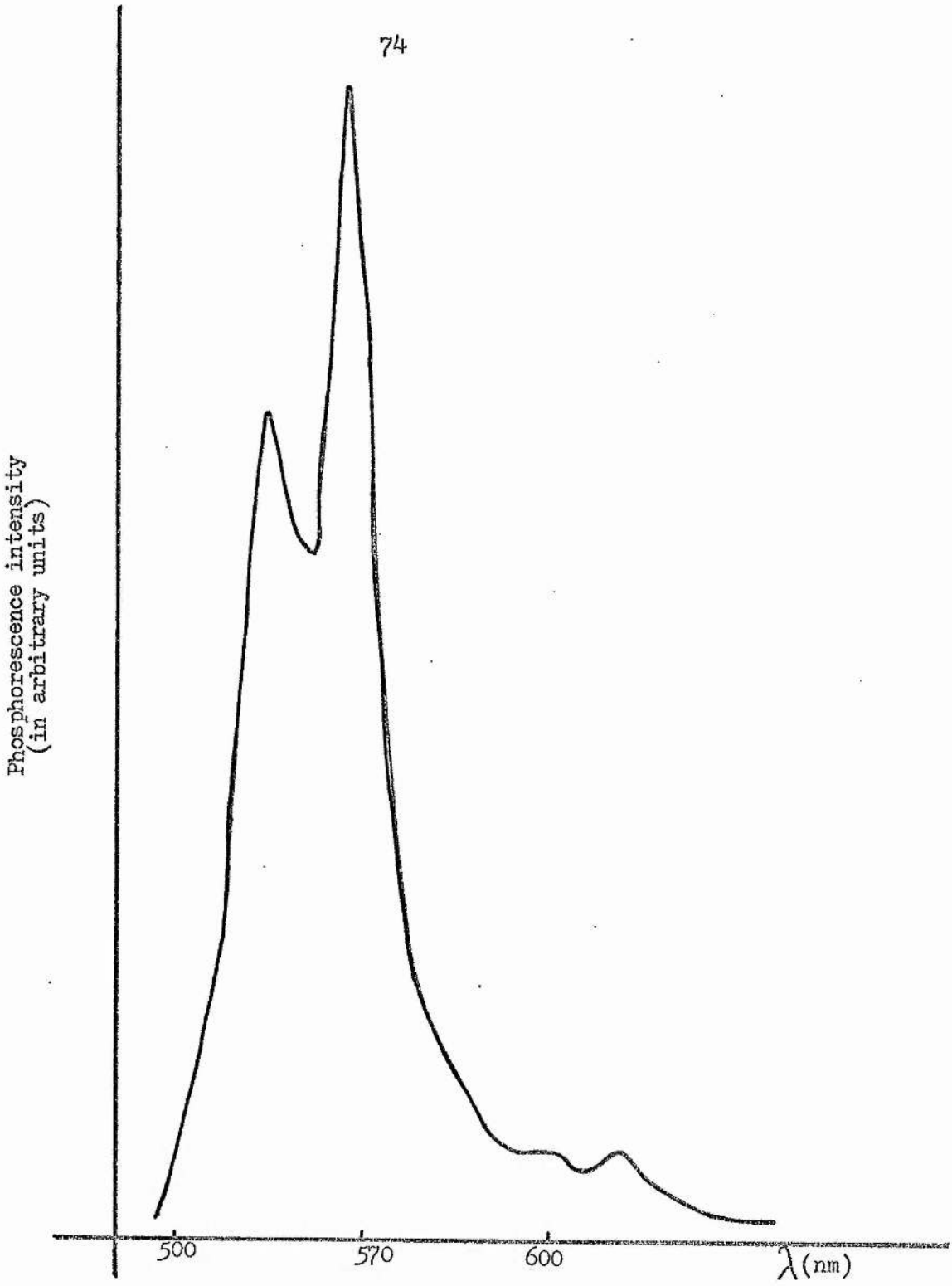


Figure 3.24

Phosphorescence spectrum of coronene in PMMA at R.T. and under vacuum. Excited with radiation of wave-length 306 nm.

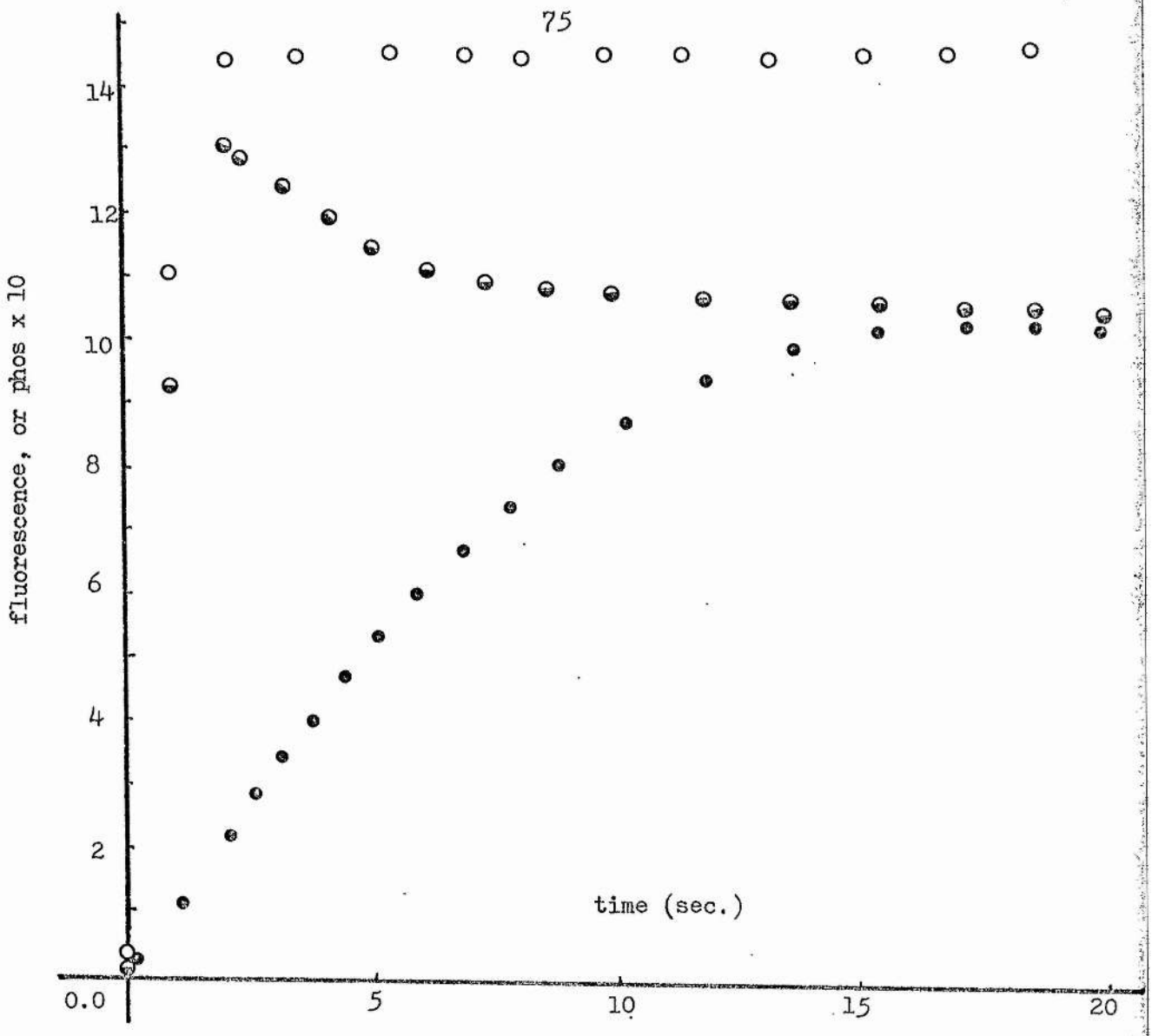


Figure 3.25

Build-up the fluorescence (⊖) and phosphorescence (●) of coronene in PMMA in vacuum, and build-up of fluorescence in O_2 (O).

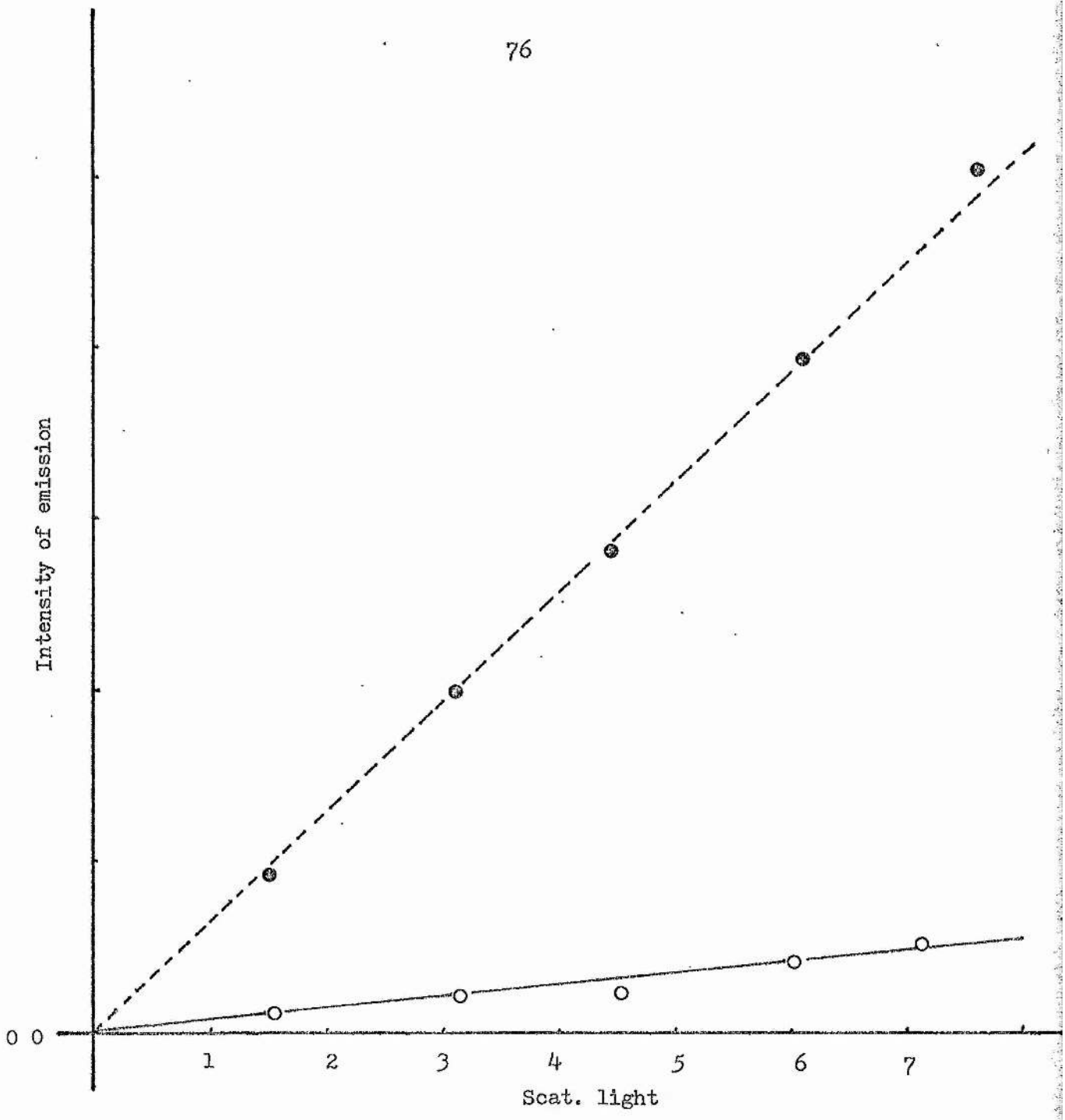


Figure 3.26

Maximum values of fluorescence, (●); and steady state values of phosphorescence, (○); for coronene in PMMA in vacuum vs. intensity of scattered light.

TABLE 3.7

τ of coronene at different conditions.

Matrix	τ (sec.) R.T.	77K
PMMA	8.5[a]	9.5[b]
PVA	7.25	9.0
PMMA + 10^{-3} M Cys.	7.09	9.33
PMMA + 10^{-2} M DABCO	7.0	8.7

Literature values a - 6.5 sec. from ref. 34

b - 9.6 sec. from ref. 44

When O_2 was admitted to the sample of coronene in different plastic films, there resulted a rapid decrease in phos. intensity, and the fluor. intensity increased simultaneously (figure 3.23). Moreover, when O_2 was pumped completely from the system, the fluor. and phos. intensities returned to their original values in vacuum. Quenching the excited states of coronene by O_2 in PMMA are shown in figure 3.27 and the data are listed in Table 3.8.

Figure 3.27

Quenching the fluorescence, (●); and phosphorescence, (○); of coronene in PMMA by O_2.

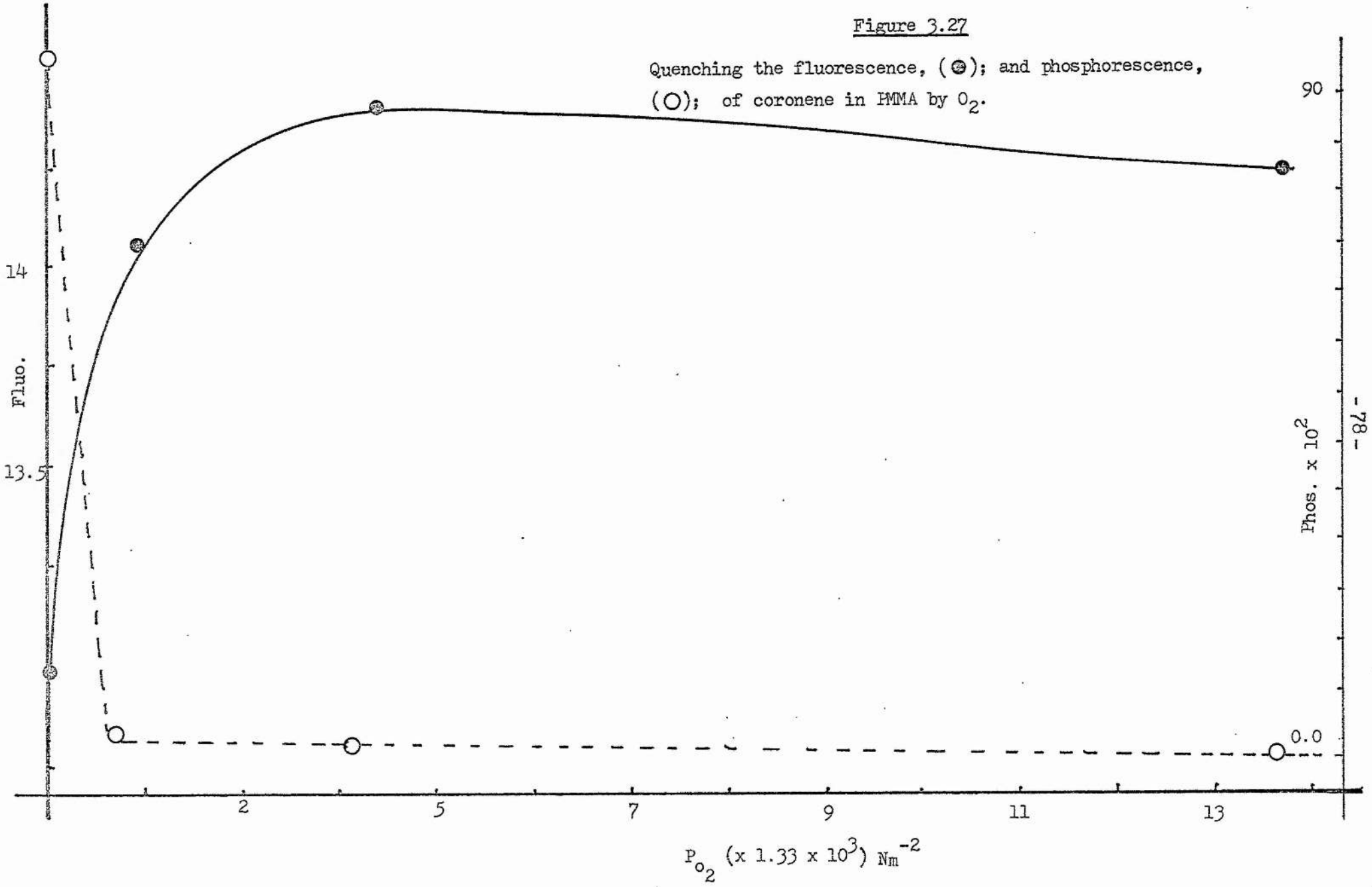


TABLE 3.8

Quenching excited states of coronene

by O_2 in PMMA matrix

P_{O_2} (1.33×10^3 N m^{-2})	Relative intensity of fluor. (at maximum)	Relative intensity of phos.
0.0	12.96	0.97
0.872	14.02.	0.03
3.32	14.36	0.0
12.78	14.25	0.0
27.072	14.11	0.0
34.964	13.94	0.0
49.7	13.84	0.0
67.8	13.72	0.0

Stern-Volmer treatment for fluor. intensities against O_2 pressure yielded a similar S/V plot to that outlined for triphenylene in PMMA (figure 3.28). The linear part of the plot was extrapolated and I_{extr} was obtained. A good S/V plot was obtained when I_{extr}/I_e plotted versus P_{O_2} as presented in the above figure.

The results of similar quenching studies in Pst are listed in Table 3.9 and shown in figure 3.29, along with that in PMMA for the purpose of comparison.

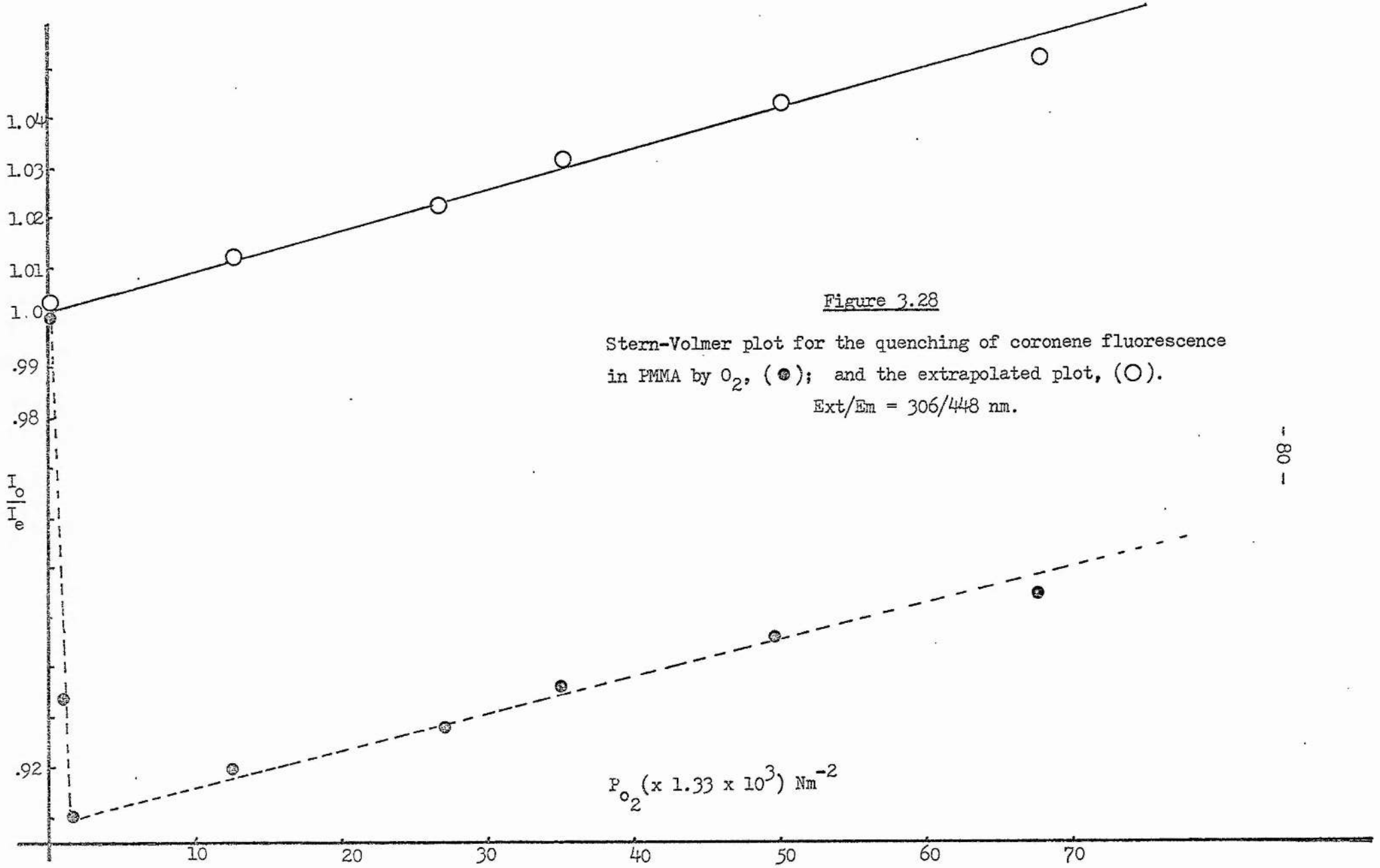


Figure 3.28

Stern-Volmer plot for the quenching of coronene fluorescence in PMMA by O_2, (●); and the extrapolated plot, (○).
Ext/Em = 306/448 nm.

Figure 3.29

S/V plot for quenching COR. fluorescence by O_2 in PMMA(●) and in Pst (○).

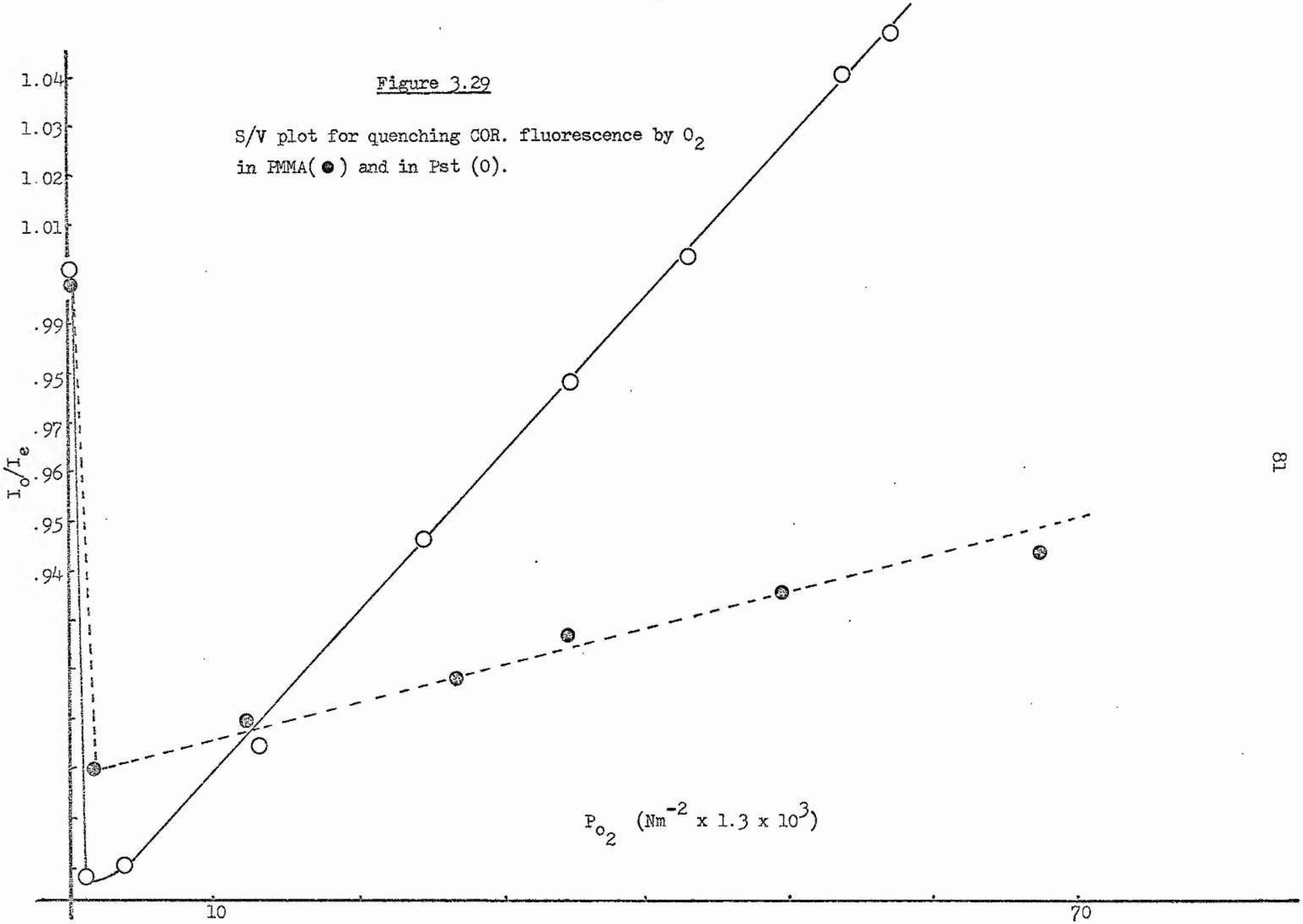


TABLE 3.9

Quenching the excited states of coronene by O_2 in Pst matrix

$P_{O_2} \times (1.33 \times 10^3) Nm^{-2}$	Relative intensity of fluor.
0.0	11.01
1.00	12.55
4.00	12.53
13.80	12.06
24.70	11.66
34.90	11.26
43.00	10.94
53.90	10.6
62.00	10.33
70.2	10.06

The gradients of the linear parts of S/V plots were found to be $5 \times 10^{-7}\ m^2\ N^{-1}$ (corr. 0.995) and $2.4 \times 10^{-6}\ m^2\ N^{-1}$ (corr. 0.999) in PMMA and in Pst respectively. Considering that coronene fluor. lifetime in Pst is equal to that in PMMA, 300 ns[38], the quenching rate constant multiplied by the distribution constant, $k_q K$ was found to be $1.8\ m^2\ N^{-1}\ s^{-1}$ in PMMA and $8\ m^2\ N^{-1}\ s^{-1}$ in Pst.

Nitric oxide "NO" was used to quench the excited states of coronene. Admission of a low pressure of NO, 1333.22 Nm^{-2}, to an evacuated cor/PMMA system resulted in increasing the fluor. and decreasing the phosphorescence slowly. At this pressure the phos. decay was observed to be exponential with a decay time of 2.4 sec. When traces of O_2 added to cor/PMMA (using oil pump only) reduced the life time to 1.8 sec. and the phos. decay was found to be almost exponential (figure 3.30). Figure 3.31 shows the quenching of coronene phos. by NO together with that by O_2 for the sake of comparison.

The cor/PMMA system was left in a low pressure of O_2 so that all the triplets were quenched. Subsequently 1.33×10^4 Nm^{-2} of O_2 were admitted and a decrease in fluorescence intensity was observed.

The phosphorescence life time of coronene was measured in different St-MMA copolymers and the results are collected in Table 3.10.

TABLE 3.10

The phos. life time of coronene in St-MMA copolymers

Mole fraction of styrene unit	R.T. τ (sec.)	R.T. $^o\tau/^s\tau$	77K τ (sec.)	77K $^o\tau/^s\tau$	$\left(\frac{I_f}{I_p}\right)_{R.T.}$
0.0 (PMMA)	8.3[a]	1	9.4[b]	1	10.1
0.1875	6.75	1.229	9	1.044	-
.5807	7	1.185	8.85	1.0621	15
1.00 (Pst)	6.2[c]	1.338	7.71[d]	1.21	18

Literature values

a - 6.5 sec. from ref. 34

b - 9.6 sec. from ref. 44

c - 5.67 sec. from Ref. 44

d - 8.3 sec. from Ref. 44

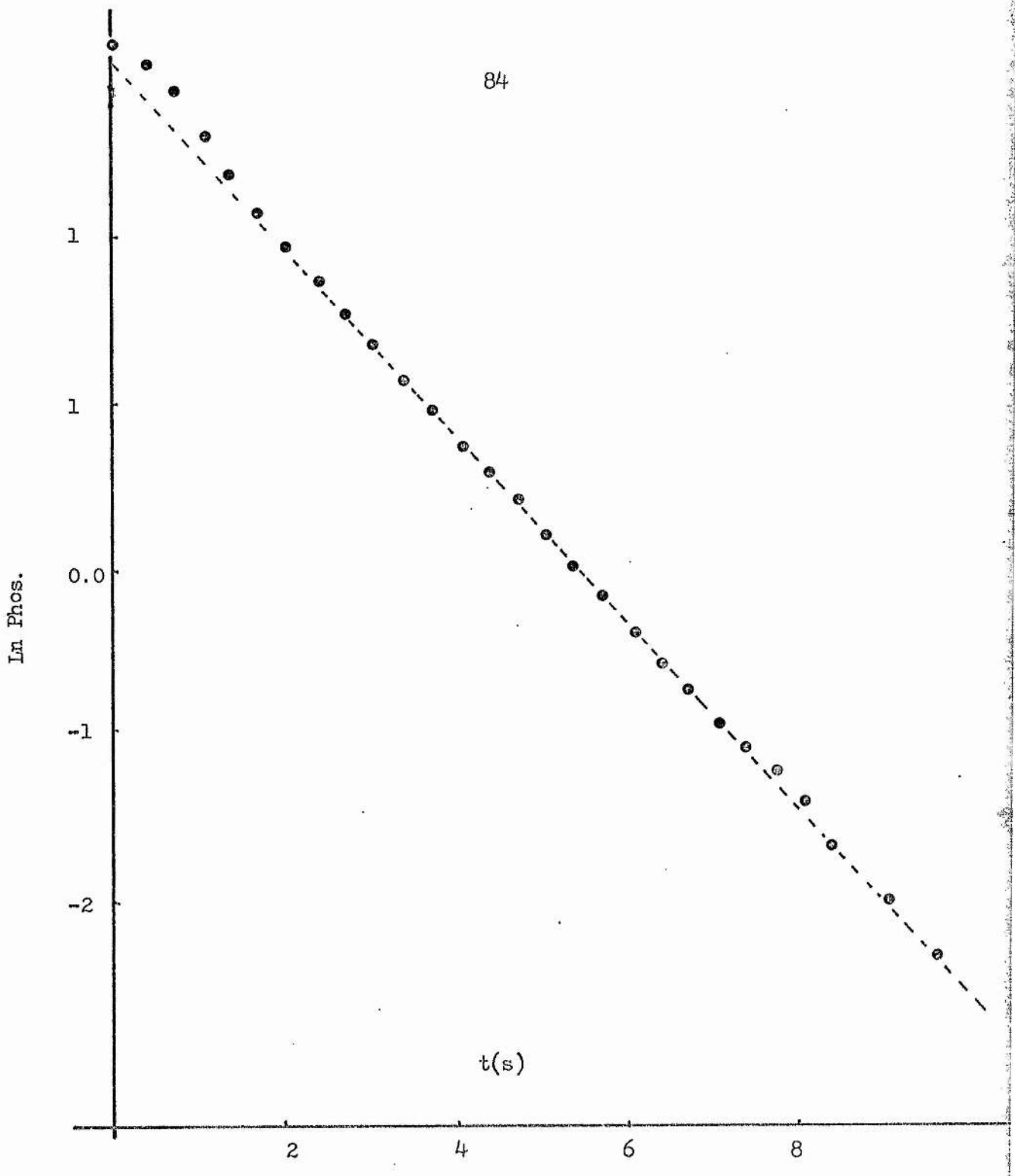


Figure 3.30

Decay of COR. phosphorescence under O_2 in PMMA.

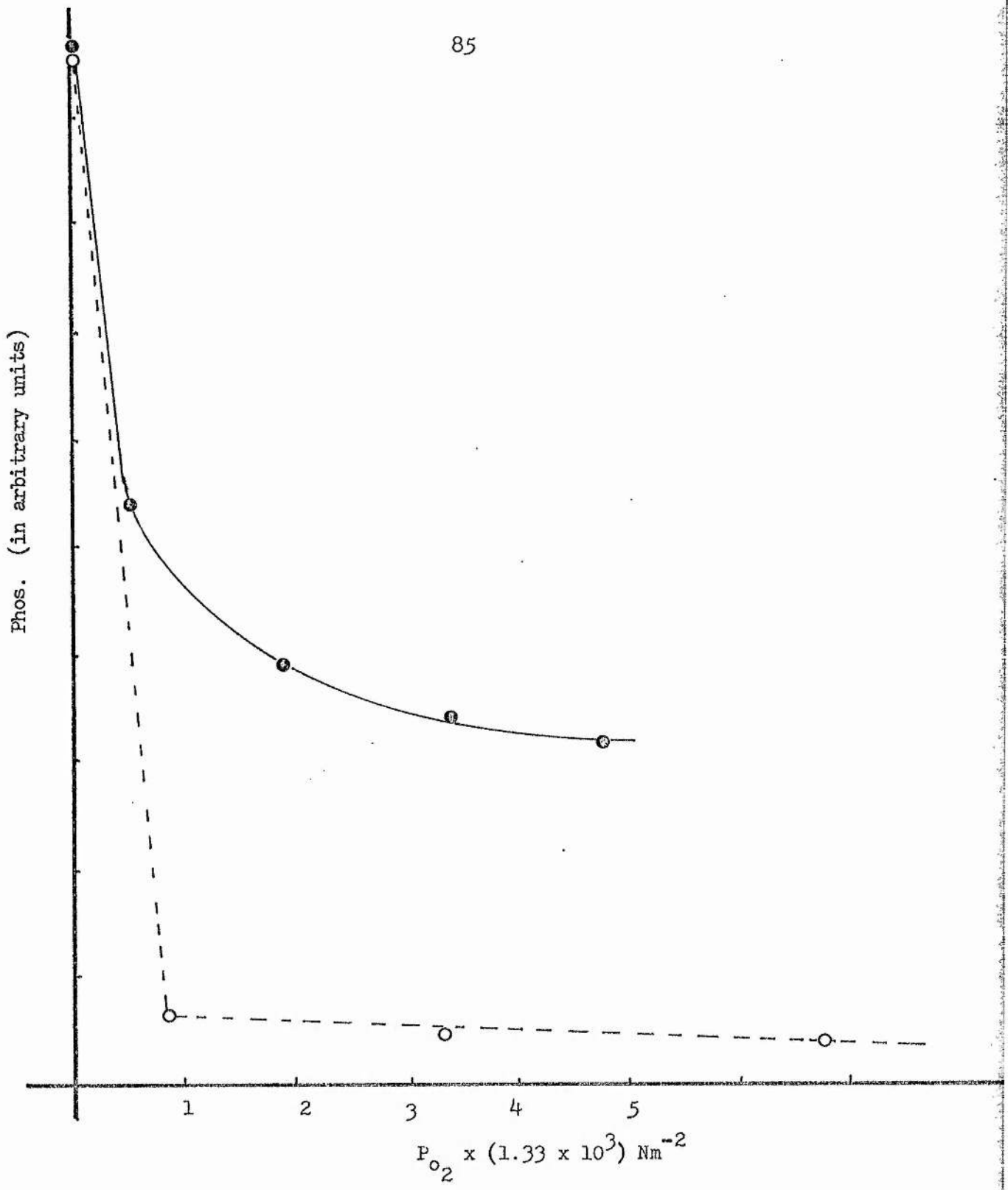


Figure 3.31

Qhenching the phosphorescence of COR in PMMA by O_2 (O); and NO gas (●) (Normalised plot).

A Stern/Volmer type of treatment for the life time of coronene phosphorescence against mole fraction of styrene unit revealed a linear plot as shown in figure 3.32. The slope was measured and k_q evaluated at 77K (see Table 5.2).

3. Naphthalene

Naphthalene is another compound which provides the opportunity to study the behaviour of small molecules in plastics. A series of measurements were carried out on this additive in PMMA, Pst, PEMA and (EMA-MMA) co-polymers and the following results were obtained.

A - Naphthalene emits strong fluorescence and very weak phosphorescence even at 77K. Its phosphorescence spectrum is shown in figure 3.33.

B - Linear plots were obtained when fluorescence and phosphorescence plotted against intensity of scattered light (fig. 3.34).

C - Decay of phosphorescence is non-exponential under vacuum in both PMMA and Pst at R.T. and at 77K as shown in figure 3.35.

D - Table 3.11 lists its phosphorescence decay time at different conditions

Matrix	τ (sec.) this work		τ (sec.) literature value	
	R.T.	77K	R.T.	77K
PMMA	1.43	2.85	1.5	2.4 *
Pst	1.99	3.00	-	-

* From ref. (33)

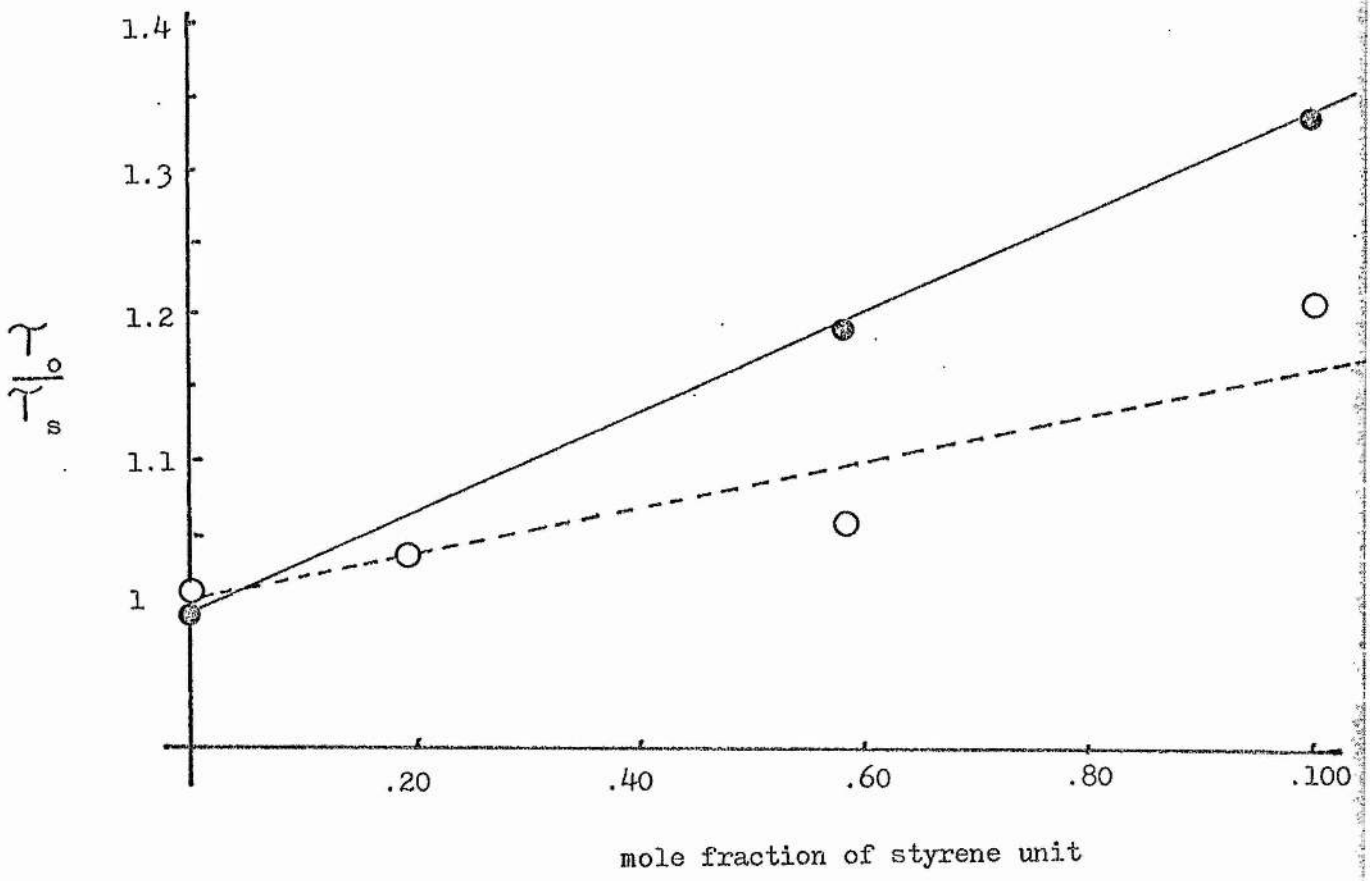


Figure 3.32

S/V plot for the quenching of COR phos.. life time by mole fraction of styrene unit in St.MMA copolymers at room temperature (⊛) and at 77K (O).

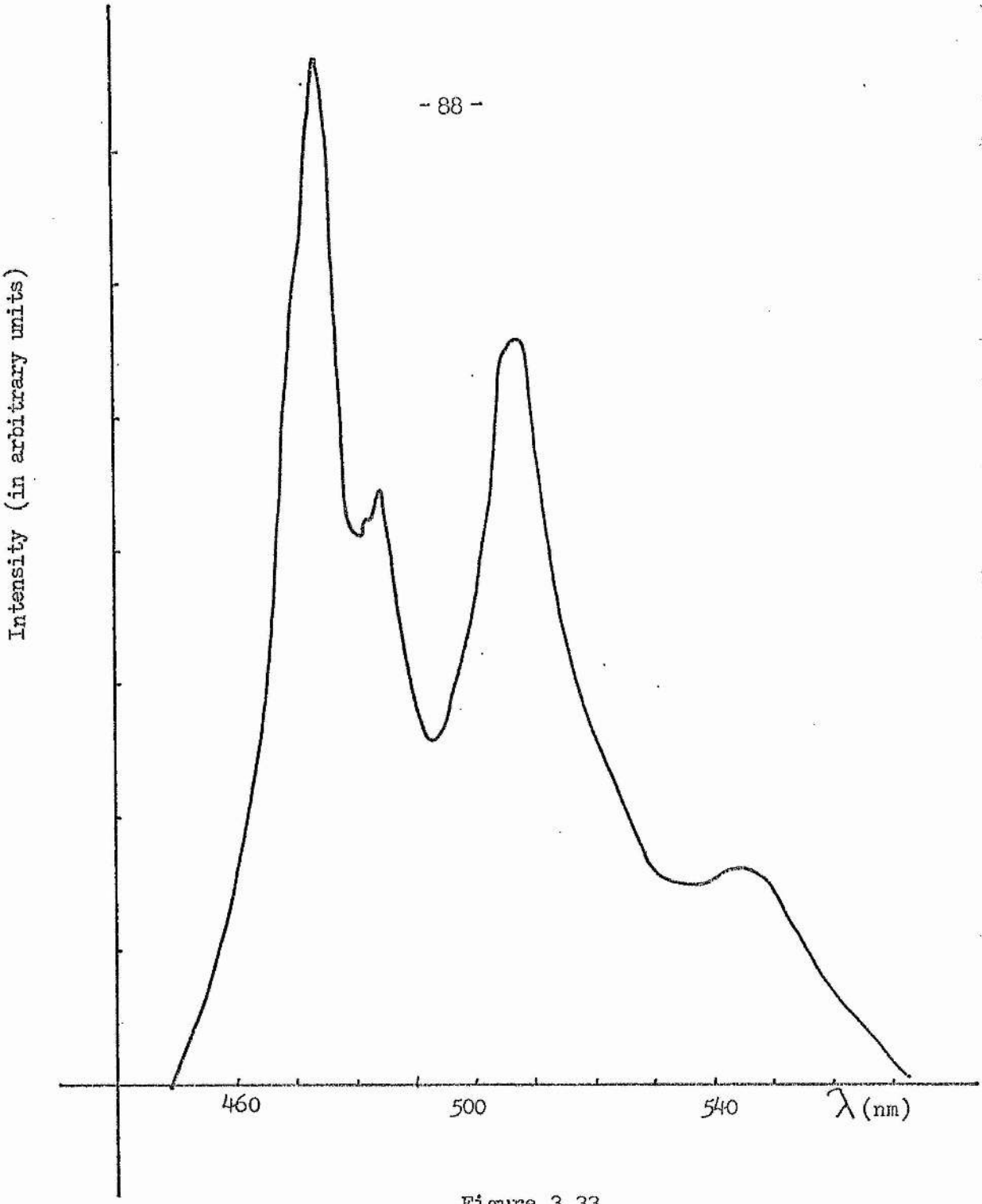


Figure 3.33

Phos. spectrum of naphthaelene in PMMA at 77K.
Excitation at 290 nm.

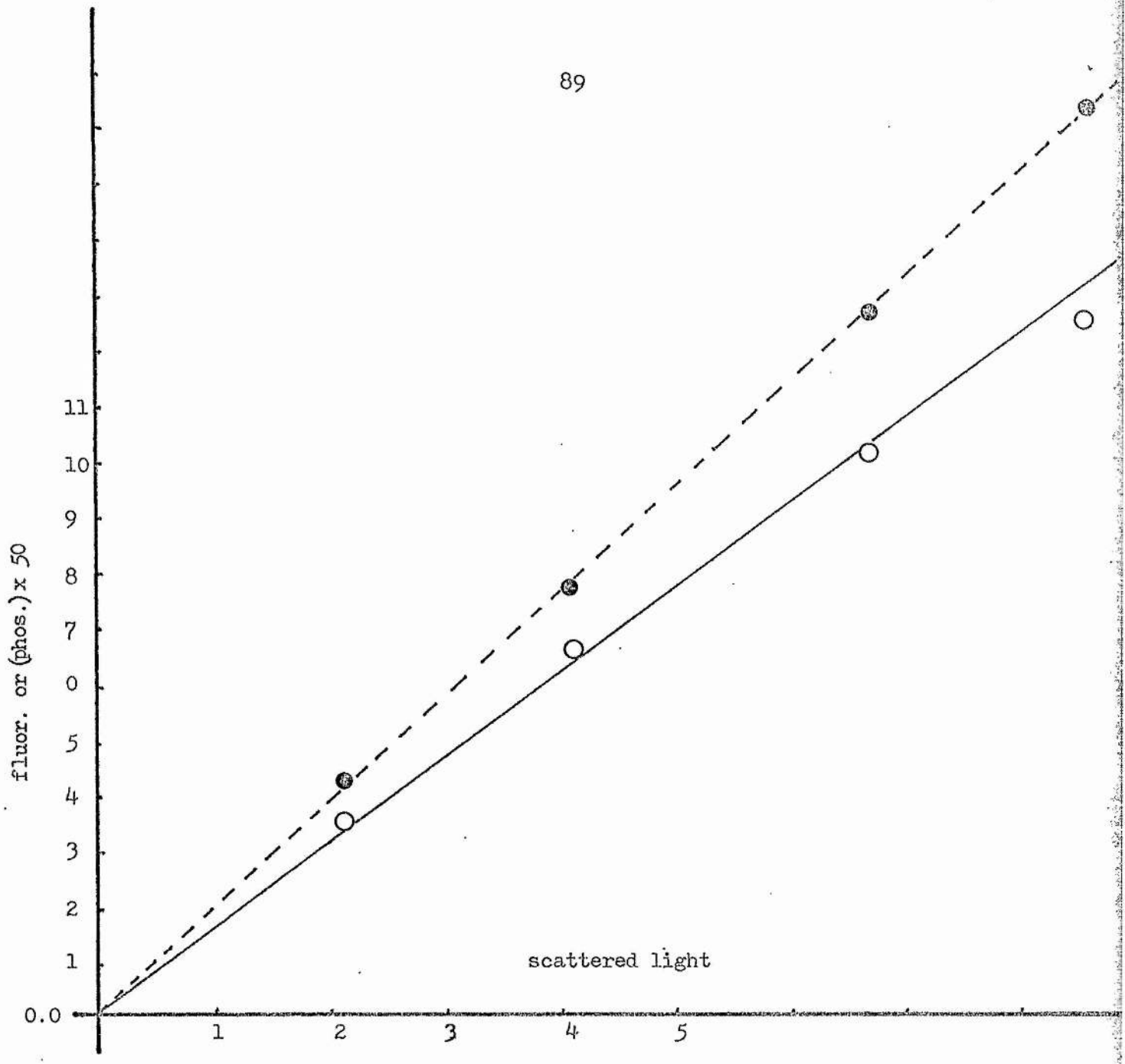


Figure 3.34

Fluorescence (●) and phosphorescence (O) intensities of naphthalene in PMMA vs. scattered light.

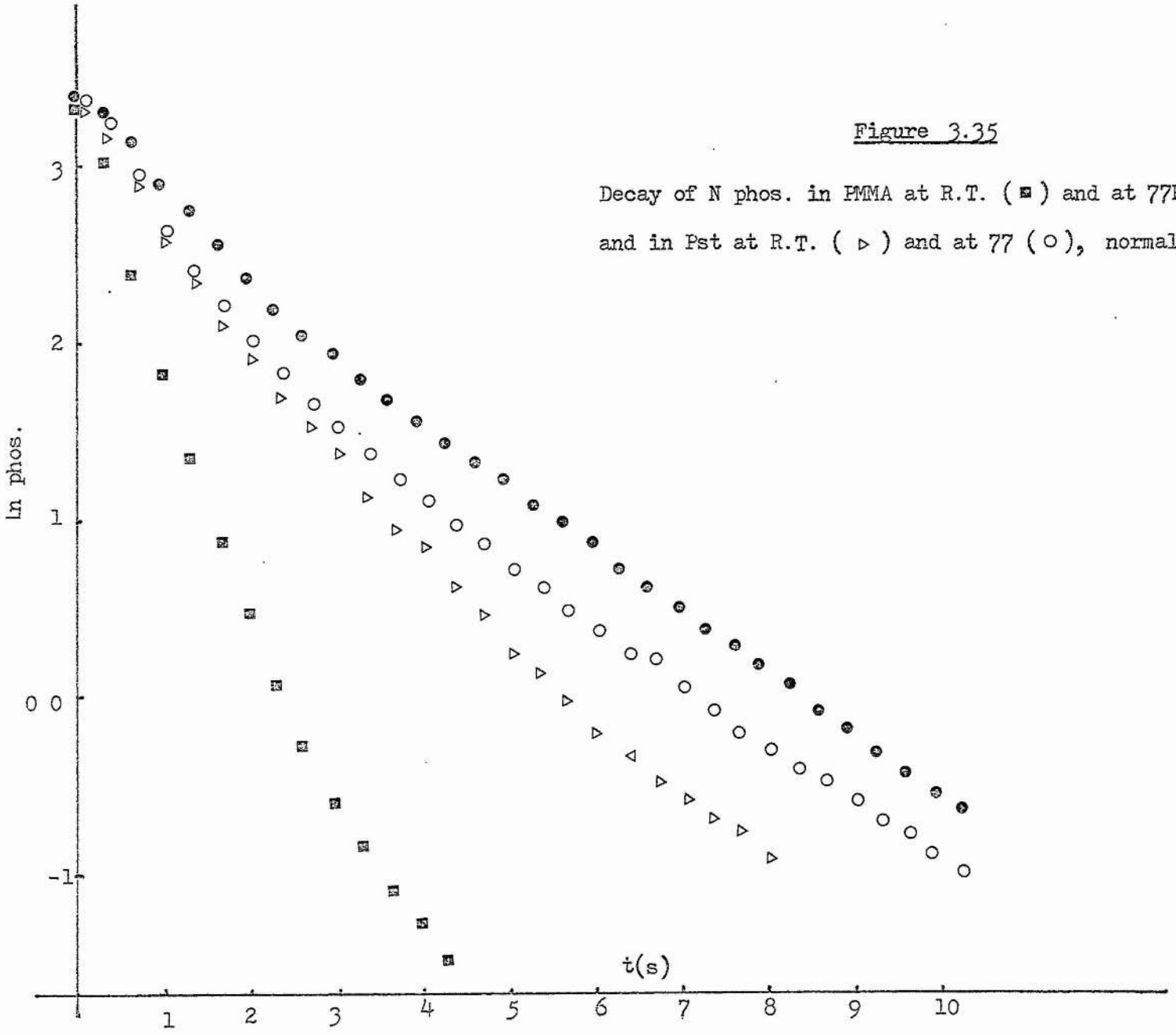


Figure 3.35

Decay of N phos. in PMMA at R.T. (▣) and at 77K (●)
and in Pst at R.T. (▷) and at 77 (○), normalised plots.

E - A good S/V plot was obtained for quenching the fluorescence of N by O_2 in PMMA and Pst and k_qK was found to be 1.2×10 $m^2 N^{-1} s^{-1}$ in PMMA and 1.55×10 $m^2 N^{-1} s^{-1}$ in Pst, accepting that the fluorescence life time of N in Pst is the same as in PMMA, 100 ns[74]. Figure 3.36, shows the process in Pst.

4. Phenanthrene

The phosphorescence spectrum of phenanthrene at R.T. is shown in figure 3.37. It was found that the phos. decay was almost exponential in both PMMA and Pst at R.T. and at 77K, whereas it was totally exponential under very low pressure of O_2 with a life time of 0.65 sec. Values of phos. decay time are collected in Table 3.12.

TABLE 3.12

Phos. life time of phenanthrene

Matrix	τ (sec.) this work		$\tau_{(s)}$ literature value	
	R.T.	77K	R.T.	77K
PMMA	2.9	3.77	2.5	3.8 *
Pst	2.38	3.46	-	-

* From ref. 33

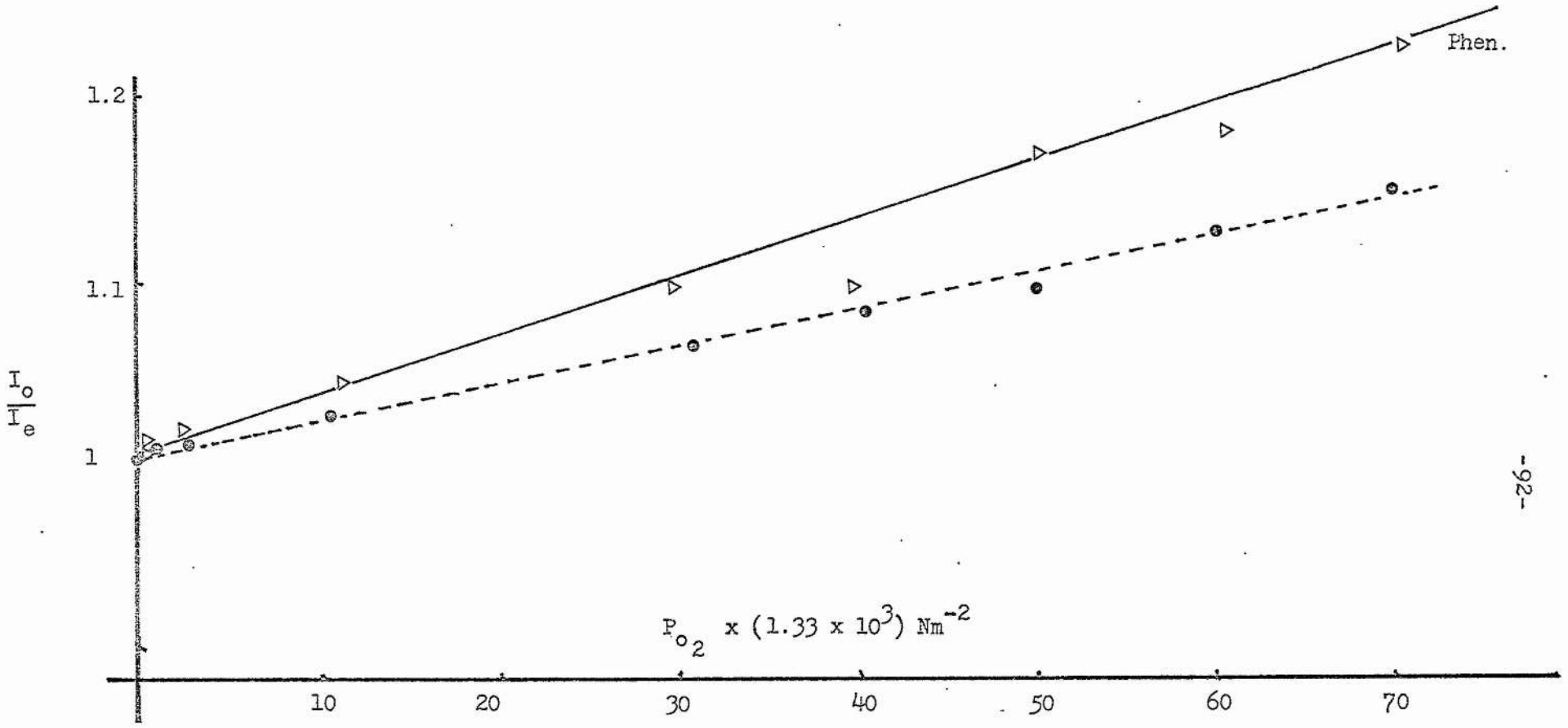


Figure 3.36

S/V plots for quenching the fluorescence of Phen. (▷) (Ext/Em = 300/368 nm) and of naphthalene (●) (Ext/Em = 280/336 nm) in Pst by O_2.

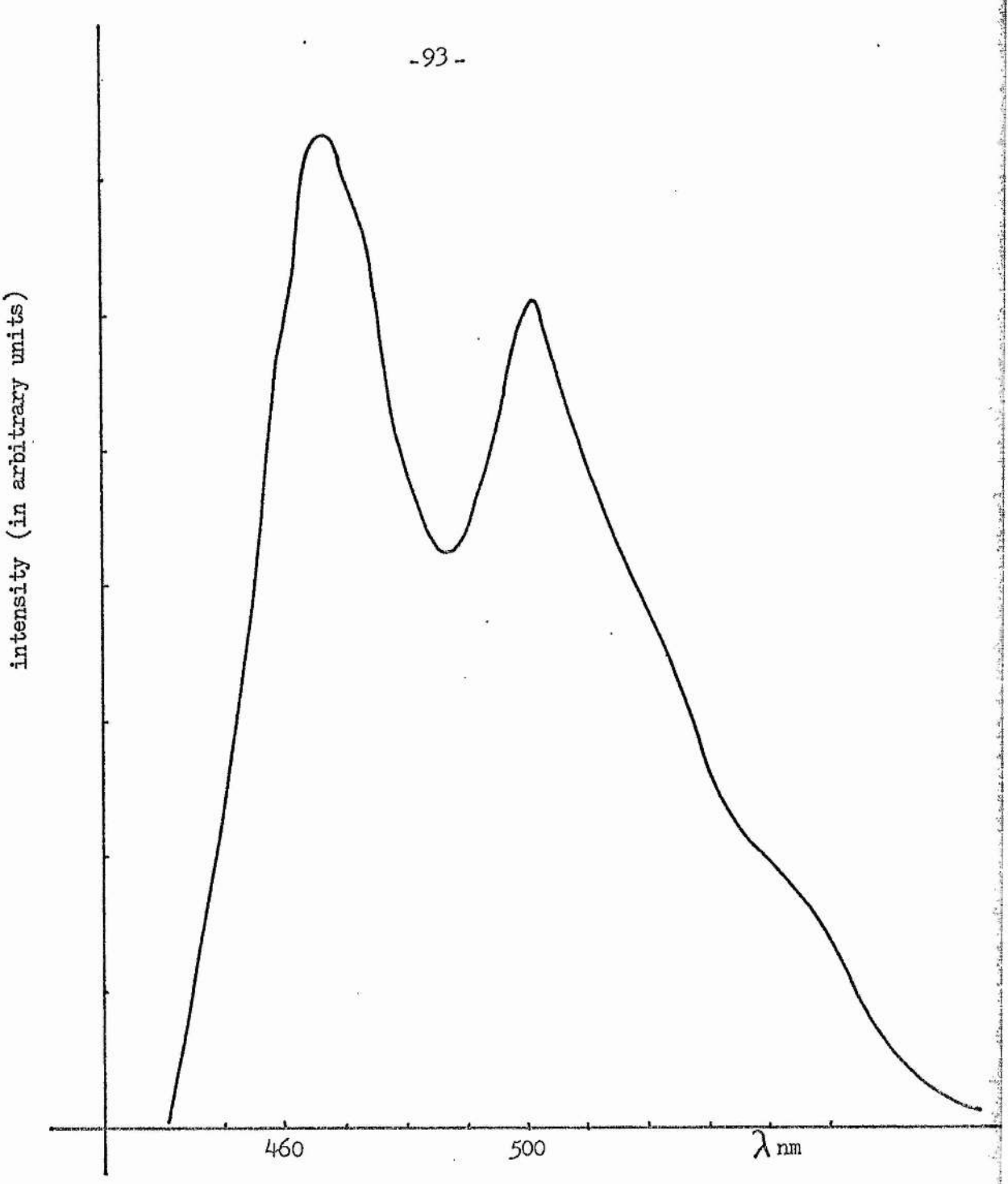


Figure 3.37

Phos. spectrum of phen. in PMMA at room temperature, excitation at 260 nm.

It has been found that the plots of fluor. and phos. against intensity of scattered light are straight lines (at low intensity of light) passing through the origin, see figure 3.38, and I_f/I_p was found to be 16 in PMMA at R.T.

Finally, a good S/V plot was obtained for fluor. quenching by O_2 in Pst matrix (figure 3.36), and k_qK was found to be 4.2×10 $m^2 N^{-1} s^{-1}$, considering its life time as in PMMA, 56 ns.(74).

5. Perylene

Perylene provides the opportunity to study quenching of fluor. of a compound which has a relatively short life time (6.7 ns in solution)(13). Assuming the life time is the same as in PMMA matrix, k_qK was found to be 1.2×10^2 $m^2 N^{-1} s^{-1}$ as calculated from the S/V plot which is shown in figure 3.39.

All values for k_qK in polymer films at R.T. are collected in Table 3.13 for purpose of comparison.

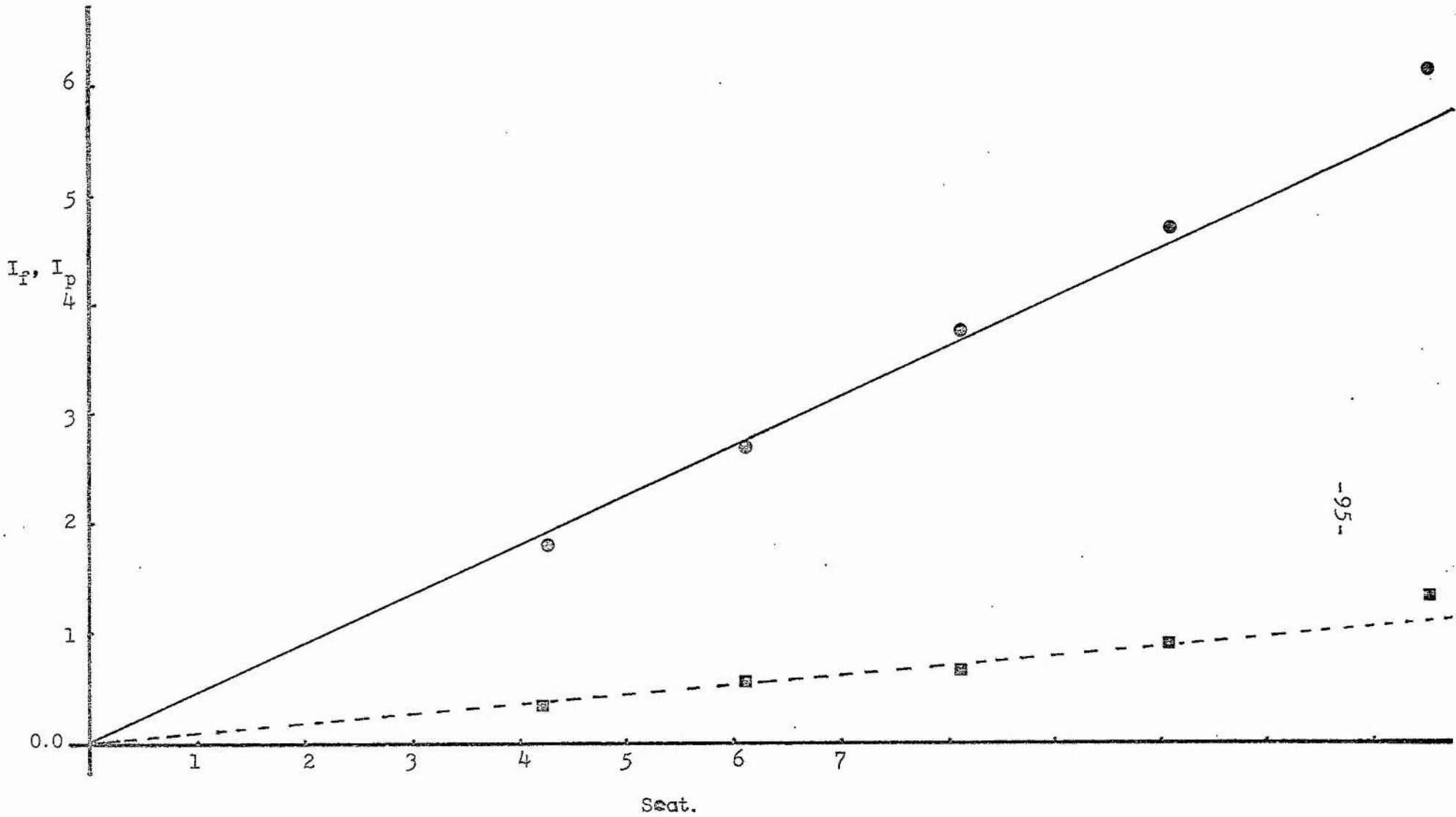


Figure 3.38

Fluorescence (●) and phosphorescence (■) intensities of phenanthrene in PMMA vs. scattered light.

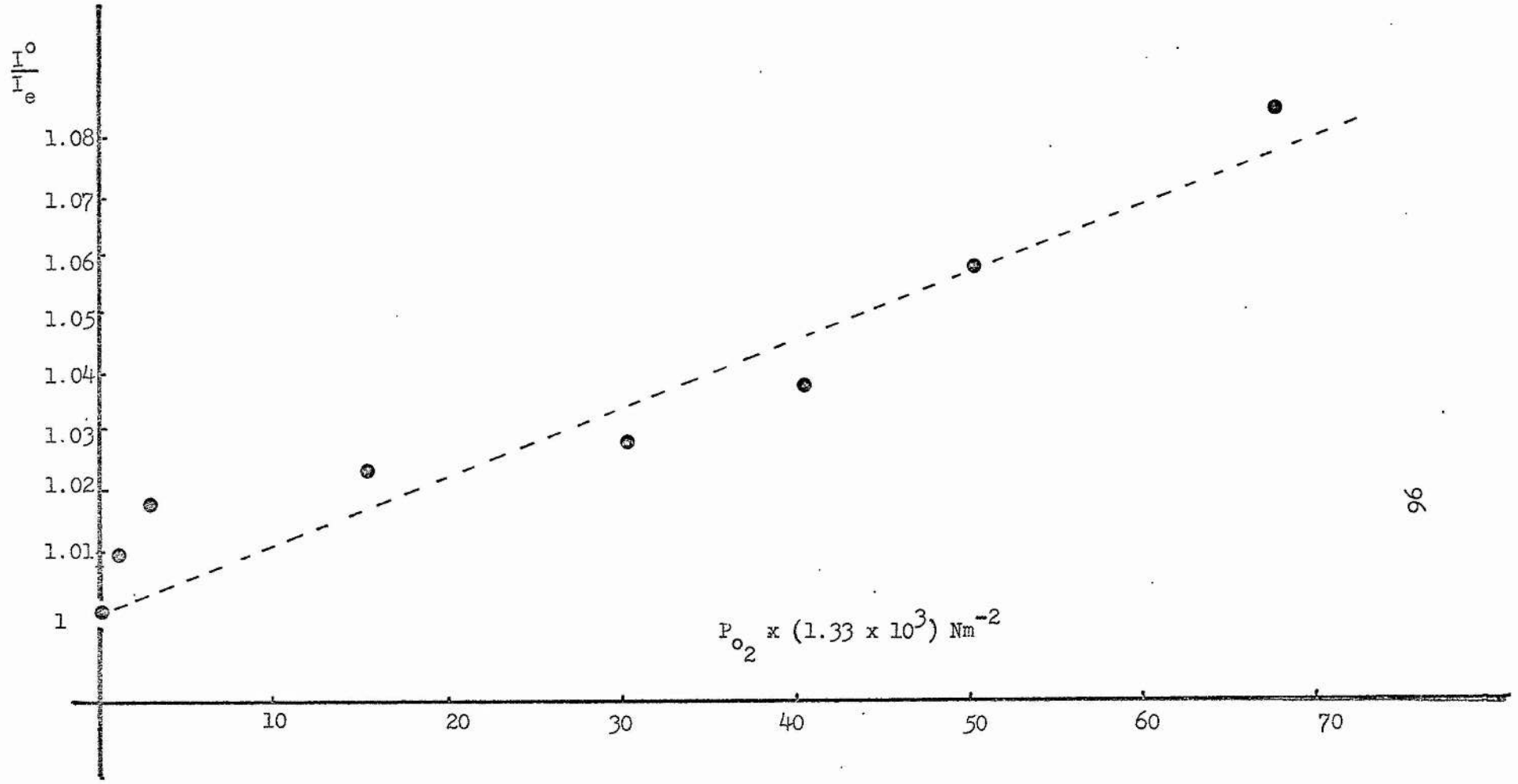


Figure 3.39

Stern-Volmer plot for the quenching of Perylene fluorescence by O_2 in PMMA. Ext/Em. = 260/470 nm.

TABLE 3.13

Aromatic	Matrix	Fluorescence life time (ns)	$k_q K$ ($m^2 N^{-1} s^{-1}$)
P	PMMA	6.7[a]	1.2×10^2
Tri	PMMA	37[b]	1.3 x 10
	PEMA		1.7 x 10
	(EMA/MMA) 60%		9.4 x 10
Phen.	Pst	56[b]	4.24 x 10
N	PMMA	100[b]	1.2 x 10
	Pst		1.55 x 10
COR	PMMA	300[c]	1.8
	Pst		8.0

Literature values. a - in nitrogenated cyclohexane, ref. 13

b - from ref. (74) at R.T. in PMMA

c - in PMMA at R.T., ref. (38)

III Quenching of the fluorescent polymers.

Stern-Volmer plots for quenching the fluorescence of Pst and Pαmst films by O_2 are shown in figures 3.40 and 3.41.

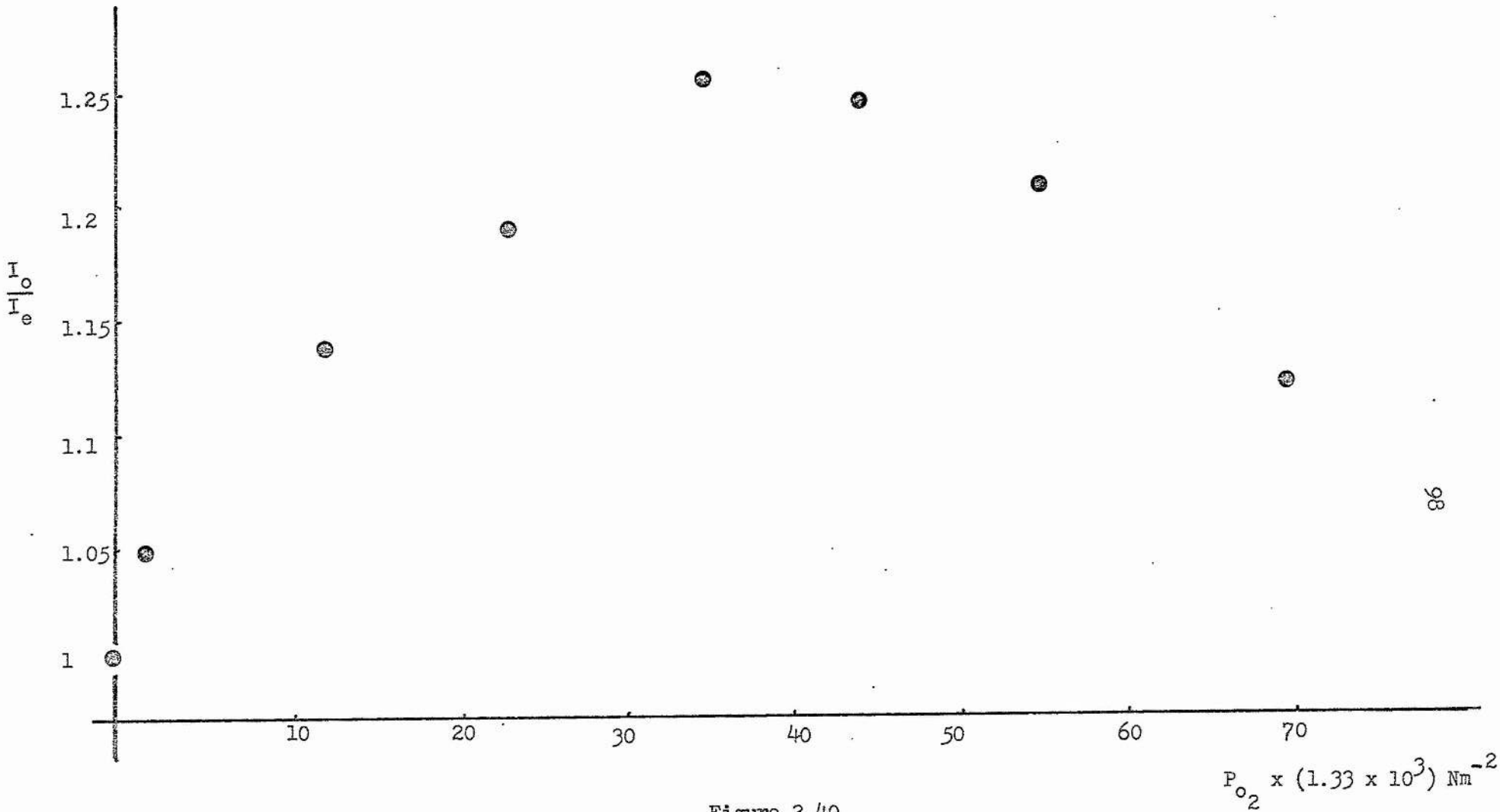


Figure 3.40

Stern-Volmer plot for quenching the fluorescence of thin Pst film by O_2. Ext/Em. = 260/330 nm.

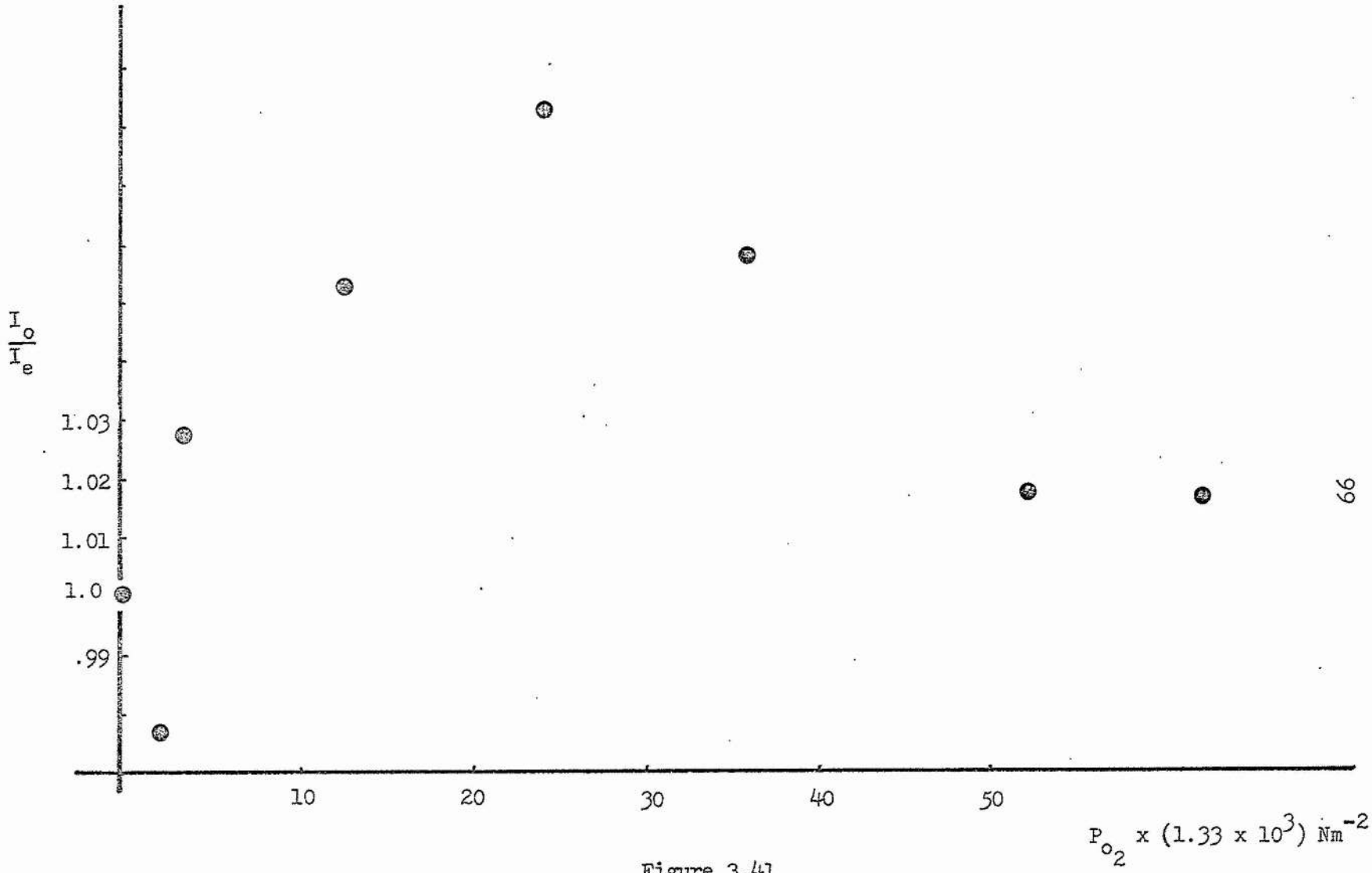


Figure 3.41

Stern-Volmer plot for the quenching of the fluorescence of P∝mst film by O_2. Ext/Em. = 260/334 nm.

IV Quenching in solution by DABCO

The fluorescence of aromatic hydrocarbons was quenched in solution by DABCO. Toluene was used as a solvent, and the concentration of DABCO varied from 5×10^{-5} M to 5×10^{-2} M.

Naphthalene, phenanthrene, perylene and anthracene were found to show good S/V plots, Figure 3.42. Coronene exhibited anomalous behaviour similar to that in rigid PMMA when quenched by O_2, however the linear part was used in our calculations. The values of the quenching rate constant, k_q, which was obtained from the gradients of S/V plots, in air and in N_2 are indicated in Table 3.14 together with the fluorescence life times.

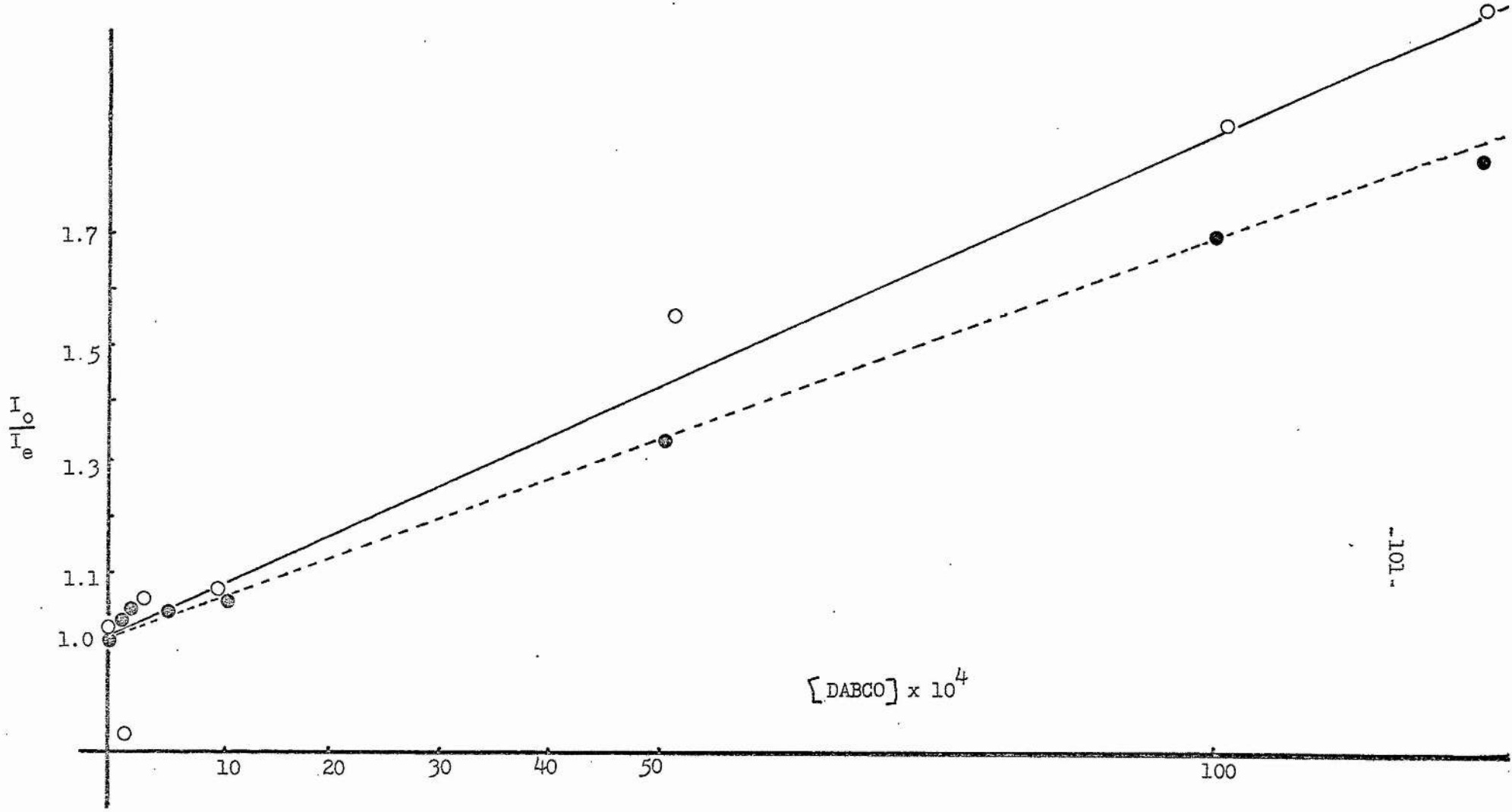


Figure 3.42

S/V plots for quenching the fluor. of naphthalene 7.8×10^{-3} M , (○); and phenanthrene 1.1×10^{-3} M , (●), by DABCO in toluene.

TABLE 3:14

Quenching of excited singlet states by DABCO in toluene

Aromatics	Concentration [M]	$\frac{N_2 I_o}{air I_o}\left(\frac{\tau_{N_2}}{\tau_{air}}\right)^a$	τ_f (ns) N_2	τ_f (ns) air	k_q ($M^{-1} s^{-1}$) N_2	k_q ($M^{-1} s^{-1}$) air	Literature value for k_q in methanol in air[e]
Anthracene	1.7×10^{-3}	1.58	4.2[b]	2.65	2.1×10^{10}	2.1×10^{10}	4.78×10^9
Perylene	6.3×10^{-4}	1.78	5.5[b]	3.00	1.83×10^{10}	1.80×10^{10}	-
Phenanthrene	1.1×10^{-3}	3.8	57.5[c]	15.13	1.14×10^{10}	4.56×10^9	7.58×10^8
Naphthalene	7.8×10^{-3}	5.88	110[b]	18.7	4.8×10^9	4.9×10^9	2.75×10^9
Coronene	5×10^{-5}	9.42	300[d]	31.84	1.74×10^7	3.5×10^8	-

Literature value.

a - Berlman method (ref. 13)

b - measured in toluene, ref. (139)

c - measured in nitrogenated cyclohexane, ref. (13)

d - measured in PMMA at R.T., ref. (38)

e - From ref. (125)

V Depolarisation measurements

In this work an attempt was made to use the depolarisation measurements as a further tool to observe the influence of concentration, temperature and media on the photophysical behaviour of aromatic investigated. Depolarisation measurements were made on films using equation 2.2 at the sharp peak maximum. Table 3.15 summarises the results.

TABLE 3.15

Depolarization measurements

1. Aromatics in thin polymer film

A. Triphenylene

System	Emission	Conditions	p^{-1}
Tri/PMMA	Fluor. Ext/Em. = 260/356 nm.	-196°C	4.15
		R.T.	7.12
		R.T. at different pressures of O_2	6.22
		at 56.3°C	2.9
	Phosphorescence (260/466) nm.	-196°C	7.7
		R.T.	-5.61
		at 56.3°C	2.7
		at 70°C	-7.6
		at 84.9°C	8.5
Tri/PVA	Fluor.	0°C	2
		R.T.	7.8
	Phos.	R.T.	-4.0

Tri/PEMA	Fluo.	R.T., low intensity of irradiation (L.I.)	4.86
		R.T., high intensity of irradiation (H.I.)	6.9
		at -196°C	1.95
	Phos.	R.T., L.I.	-6.32
		R.T., H.I.	-6.25
		at -196°C	9.28
Tri/P mst	Fluo. (300/356) nm	R.T.	5.7
Tri/(St- mst) block copolymer	Fluor. (270/356) nm	R.T.	8.67
	(300/372) nm	R.T.	7.23
Tri/(St-MMA) 5%	Fluo. (290/354) nm	R.T., L.I.	10.25
		R.T., H.I.	13.4
		at -196°C, L.I.	7.01
		at -196°C, H.I.	7.3
	Phos. (290/466) nm.	R.T., L.I.	-9.46
		R.T., H.I.	-9.94
		at -196°C, L.I.	-9.96
		at -196°C, H.I.	+9.0
Tri/(EMMA-MMA) 20%	Fluo. (260/355) nm.	R.T., L.I.	2.46
		R.T., H.I.	2.35
	(260/360) nm.	at -196°C, L.I.	2.9
		at -196°C, H.I.	1.77

	Phos. (260/466) nm.	R.T., L.I.	5.76
		R.T., H.I.	3.28
	(260/460) nm.	at -196°C, L.I.	3.53
		at -196° C, H.I.	2.0
Tri/(EMA-MMA) 60%	Fluo. (260/355)	R.T., L.I.	6.1
		R.T., H.I.	6.3
		at -196°C, L.I.	2.81
		at -196°C, H.I.	3.01
	Phos. (260/466)	R.T., H.I.	-6.25
		R.T., L.I.	-6.5
		at -196°C, H.I.	32.01
		at -196°C, L.I.	21.24
Tri/(EMA-MMA) 60% [c] = 10^{-1} M	Fluo. (290/359)	R.T., L.I.	15.28
		R.T., H.I.	12.94
		R.T., $P_{O_2} = 2.9 \times 10^3$ Nm^{-2}	8.45
		R.T., $P_{O_2} = 1.2 \times 10^4$ Nm^{-2}	4.32
		at -196°C, L.I.	139.3
		at -196°C, H.I.	47
	Phos. (290/466)	R.T., H.I.	-11.5
		R.T., L.I.	-10.1
		at -196°C, H.I.	-77
		at -196°C, L.I.	-16.16

B. Coronene

Systems	Emission	Conditions	p^{-1}
COR/PMMA	Fluo. (310/448) nm.	R.T.	8.36
		R.T., $P_{O_2} = 0.66 \times 10^3$ Nm^{-2}	7.32
		R.T., $P_{O_2} = 8.8 \times 10^4$ Nm^{-2}	4.83
	phos. (310/566) nm.	R.T.	-5.1

C. Naphthalene

System	Emission	Condition	p^{-1}
N/PMMA	Fluor. (280/336) nm.	R.T.	2.6
		R.T., $P_{O_2} = 0.66 \times 10^3$ Nm^{-2}	6.6
		R.T., $P_{O_2} = 8 \times 10^4$ Nm^{-2}	5.8
		at -196°C	5.4
	phos. (280/476) nm.	R.T.	1.17
		-196°C	1.19
N/(EMA-MMA) 20%	Fluor.	R.T.	6.06
		at -196°C	6.6
N/(EMA-MMA) 60%	Fluor.	R.T.	5.4
		at -196°C	5.5

D. Phenanthrene*

System	Emission	Conditions	p^{-1}
Phen./PMMA	Fluor. (260/345)	R.T.	53.81
		R.T., $P_{O_2} = 0.66 \times 10^3$ Nm^{-2}	84.33
		R.T., $P_{O_2} = 8 \times 10^4$ Nm^{-2}	14.85
	Phos. (260/466)	R.T.	77.84
Phen./PMMA (Traces)	Fluor.	R.T.	-30.16
	phos.	R.T.	-12.15
		at -196°C, H.I.	+2.2
		at -196°C, L.I.	2.91

* Depolarization of phenanthrene phos. was found to be -5.88 at both R.T. and 77K at 10^{-3}M in PMMA (ref. 138).

E. Perylene

System	Emission	Conditions	p^{-1}
P/(St-MMA) 20%	Fluor. (270/448) nm.	R.T.	1.01
P/(St-MMA) 60%	Fluo. (270/448) nm.	R.T.	6.3
	(320/448) nm.	R.T.	2.0

2. Polymers systems

A. Polystyrene

System	Emission	Conditions	p^{-1}
Polystyrene	Fluor. 260/330	R.T. at different intensities	10.5

B. Poly(α-methylstyrene)

System	Emission	Conditions	p^{-1}
Poly(α-methyl styrene)	Fluor. (260/334) nm.	R.T.	2.2
		at -196°C, L.I.	6.47
		at -196°C, H.I.	7.4
		at -196°C after the sample had been heated to 175°C	2.0
		after 80 mins. of irradiation and at the same previous conditions	2.2

CHAPTER 4

Diffusion of oxygen in polymer films

I. Introduction

Transport of small molecules, such as gases, in bulk polymers has been of intense interest to technologists and scientists for many years[126,127]. Numerous applications for polymers are critically dependent on the rate at which various molecular species are transported through them.

The literature contains several reasons for measuring the diffusion of gases through polymers, such as:

1. The diffusion of gases is of great practical importance in manufacture and processing and in subsequent use in packaging and as protective coatings[128].

2. It has been recognised for many years that the selective transport of gases through polymer films could form the basis of industrial processes for purifying gases[129].

3. It has been realised that such a measurement offers ways to probe the structure and molecular mobility of the polymer without significantly disturbing its equilibrium distribution[126].

4. The rate of diffusion of oxygen through polymer matrices is often the controlling parameter during oxidative degradation of such materials[130].

The process has been widely investigated by a number of workers using the usual pressure method[131-134]. An alternative technique for measuring the diffusion coefficient, D, of O_2 in polymer films has been reported[135], using the absorption band due to the O_2/styrene molecular complex.

More recently a simple technique for measuring D for O_2 has been reported from the laboratories of this department using the Stern/Volmer formula at low pressures of O_2. It is suitable for making measurements over a range of temperatures[130]. Although the subject has received much study, and there are many techniques available for determining D, there are few measurements at unusually low temperatures[128].

This work is directed towards developing the simple technique for measuring, D, for O_2 in polymer films at unusually high or low temperatures.

II. Theory

Since this work is based on the same principles which were used in reference 130, it will be useful as a background, to make a brief review of the field. The method is based on the fact that O_2 rapidly quenches singlet excited states. The following scheme describes the photophysical process involved:

						Rate
A	+	$h\nu$	$\longrightarrow$	$^*A$		$k_1[A]$
$^*A$			$\longrightarrow$	A +	$h\nu'$	$k_2[^*A]$
$^*A$			$\longrightarrow$	A +	heat	$k_3[^*A]$
$^*A$	+	O_2	$\longrightarrow$	A +	O_2	$k_4[^*A]\ [O_2]$

At each step, k represents a rate coefficient, A is a chromophore which may be part of a polymer molecule or an additive, and $^*A$ is the singlet excited state of A. Let, I_e, represent the number of moles of photons of emitted light per unit volume per unit time thus:

$$I_e = k_2 [^*A] \qquad 4.1$$

During constant-intensity radiation of A, and at the steady state,

$$k_1[A] = k_2[{}^*A] + k_3[{}^*A] + k_4[{}^*A][O_2] \qquad 4.2$$

from which,

$$[{}^*A] = \frac{k_1[A]}{k_2 + k_3 + k_4[O_2]} \qquad 4.3$$

Substituting for $[{}^*A]$ in reaction 4.2 and inverting gives the equation:

$$\frac{1}{I_e} = \frac{1}{k_1[A]} + \frac{k_3}{k_1k_2[A]} + \frac{k_4[O_2]}{k_1k_2[A]} \qquad 4.4$$

When all O_2 has been removed from the system, the intensity of the emitted light is at its maximum value, I_e^o, resulting in Stern-Volmer type relationship (Equation 4.5).

$$\frac{1}{I_e} = \frac{1}{I_e^o} + \frac{k_4[O_2]}{k_1k_2[A]} \qquad 4.5$$

Equation 4.5 rearranges to give equation 4.6

$$\frac{I_e^o - I_e}{I_e^o I_e} = k_5[O_2] \qquad 4.6$$

in which $k_5 = k_4/k_1k_2[A]$ 4.7

As O_2 varies from zero to the equilibrium concentration within the sample, the intensity of emitted light diminishes to a value corresponding to the final concentration of O_2; this intensity is represented by I_e^s and

$$\frac{I_e^o - I_e^s}{I_e^o I_e^s} = k_5 \left[O_2\right]_{equil.} \qquad 4.8$$

Dividing 4.6 by 4.8 gives

$$\frac{\left[O_2\right]}{\left[O_2\right]_{equil}} = \frac{\frac{I_e^o}{I_e} - 1}{\frac{I_e^o}{I_e^s} - 1} \qquad 4.9$$

The ratio $\left[O_2\right]/\left[O_2\right]_{equil.}$ can be related to the diffusion coefficient for the gas. For the conditions of a plane sheet and short times (t), the following approximation applies[128],

$$\frac{\left[O_2\right]}{\left[O_2\right]_{equil.}} = \frac{4}{L}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \qquad 4.10$$

in which L is the thickness of the film. The final relationship is:

$$\frac{\frac{I_e^o}{I_e} - 1}{\frac{I_e^o}{I_e^s} - 1} = \frac{4}{L}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \qquad 4.11$$

In this work oxygen may diffuse through the polymer film from both sides so, L, should be divided by 2 and the final equation is:

$$\frac{\frac{I_e^o}{I_e} - 1}{\frac{I_e^o}{I_e^s} - 1} = \frac{8}{L}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \qquad 4.12$$

The temperature dependence of D usually follows an Arrhenius form[126,128]

$$D = \overset{o}{D} \exp(-E/RT) \qquad 4.13$$

where $\overset{o}{D}$ and E are constant for a particular gas and polymer.

III. Experimental

The apparatus with variable temperature accessory which is described in Chapter 2 was used for diffusion measurements. We know from Chapter 3 that to get typical Stern-Volmer behaviour, we must remove all the triplets of the additive. So the initial intensity, I_e^o, at t=o was noted after the system had been left with about 9×10^3 Nm^{-2} of O_2 for enough time to quench all the triplets. The dried O_2 was then admitted carefully, so that its final pressure was of the order of 7.33×10^4 Nm^{-2}. During this period, the fall-off in the fluorescence intensity was recorded for insertion in equation (4.12) from which a value of D could be extracted by the graphical analysis. It was found that the left side of equation (4.12) is a linear function of $t^{\frac{1}{2}}$ over a short time scale. After longer emission times the plots tend to level off. A good set of data can be

obtained when a long-lived fluorescent compound (e.g. coronene) is used. Consequently, all the initial experimental data refer to a steady-state situation with the total time scale just a few minutes.

IV Results

Diffusion of oxygen in different plastic matrices was investigated over a range of temperatures. It is convenient to divide this section into several parts, according to the matrices investigated.

1. Polystyrene

Diffusion of oxygen in polystyrene was measured at room temperature using naphthalene as guest, alternatively perylene was used as additive for measurements at -80°C. The spectrofluorimeter was connected to a data transfer unit (DTU) to punch out the intensity reading every one or two seconds. The system was first kept with 1.33×10^4 Nm^{-2} of oxygen for one hour, then gently the dry oxygen was admitted so that the total pressure was about 8×10^4 Nm^{-2} A typical set of data are shown in figure 4.1 and the results are listed in Table 4.1

Table 4.1

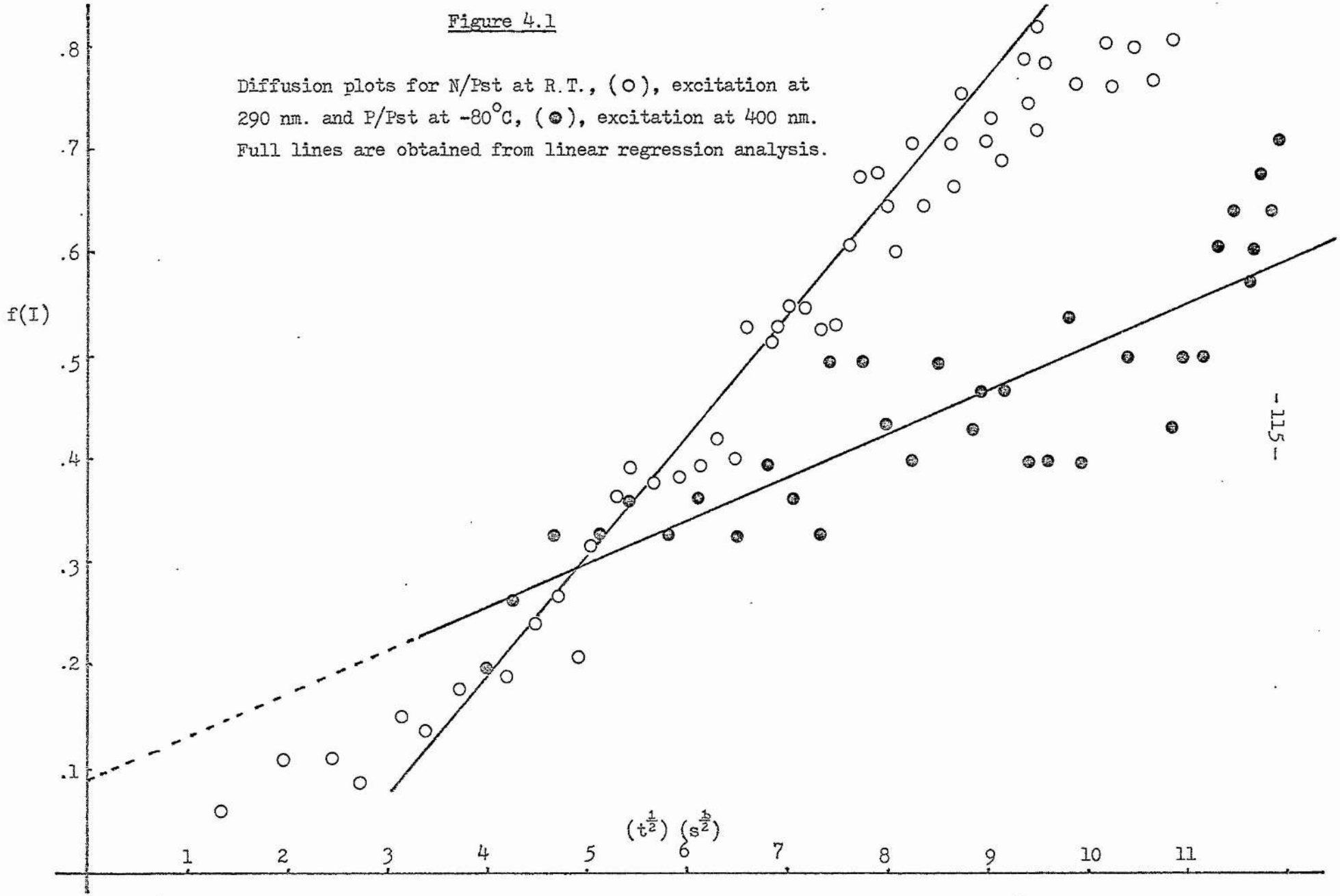
Diffusion of O_2 in polystyrene

System	Ext/Em (nm)	T(°C)	D($cm^2 s^{-1}$) this work	D($cm^2 s^{-1}$) literature
N/Pst	290/336	28	2.97×10^{-8}	1.31×10^{-8} *
P/Pst	400/474	-80	1.3×10^{-9}	———

* From ref. 130

Figure 4.1

Diffusion plots for N/Pst at R.T., (○), excitation at 290 nm. and P/Pst at -80°C, (●), excitation at 400 nm. Full lines are obtained from linear regression analysis.



2. Polymethylmethacrylate (PMMA)

A film of coronene in PMMA was used to measure D of O_2 in PMMA matrix at room temperature and at 0°C. The results are shown in figure 4.2 and tabulated in Table 4.2.

Table 4.2

Diffusion of O_2 in PMMA

System	Ext/Em (nm)	T(°C)	D(cm^2 s^{-1}) This work	D(cm^2 s^{-1}) literature
COR/PMMA	310/446	28	2.43×10^{-8}	3.8×10^{-8} *
		0	5.3×10^{-9}	——

*From ref. 130

It is interesting to note that when the total pressure of O_2 was reduced to 3.44×10^4 Nm^{-2} D increased to 5.3×10^{-8} cm^2 s^{-1} when the same system was used at 28°C.

3. Polyvinylacetate (PVA)

The diffusion of O_2 in such a rubber-like polymer was measured at room temperature, coronene was used as guest. The emission decay with time was followed graphically, at a chart speed of 100 mm/min. D, was found to be 1.8×10^{-7} cm^2 s^{-1} at 28°C, and didn't change (within experimental error) when slow rate of oxygen entry was used. This value is in reasonable agreement with literature value, 0.7×10^{-7} cm^2 s^{-1} (136).

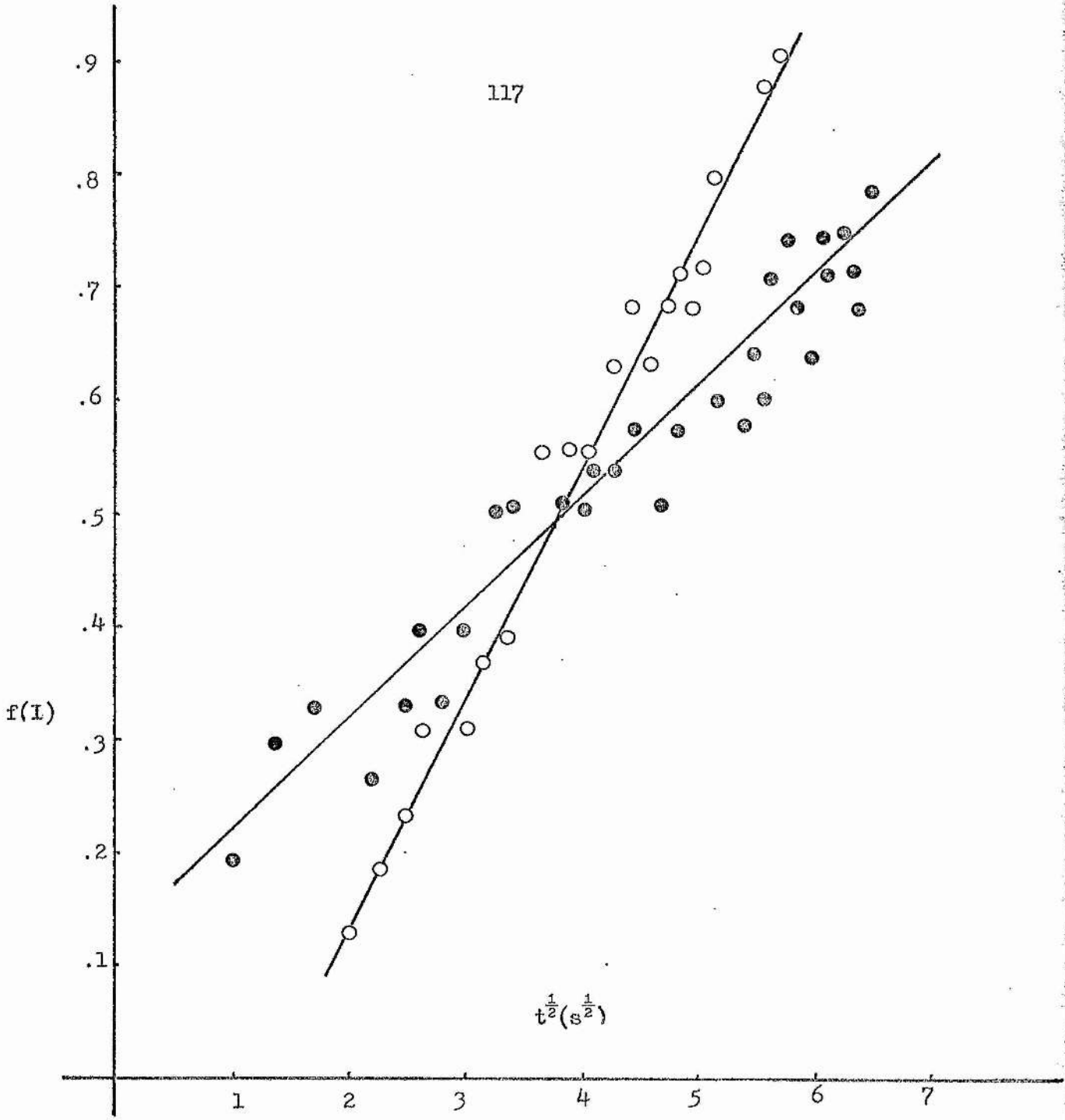


Figure 4.2

Diffusion plots for COR/PMMA at R.T., (O), and at $0^{o}C$, (⊛); Ext. at 306 nm. Full lines are obtained from linear regression.

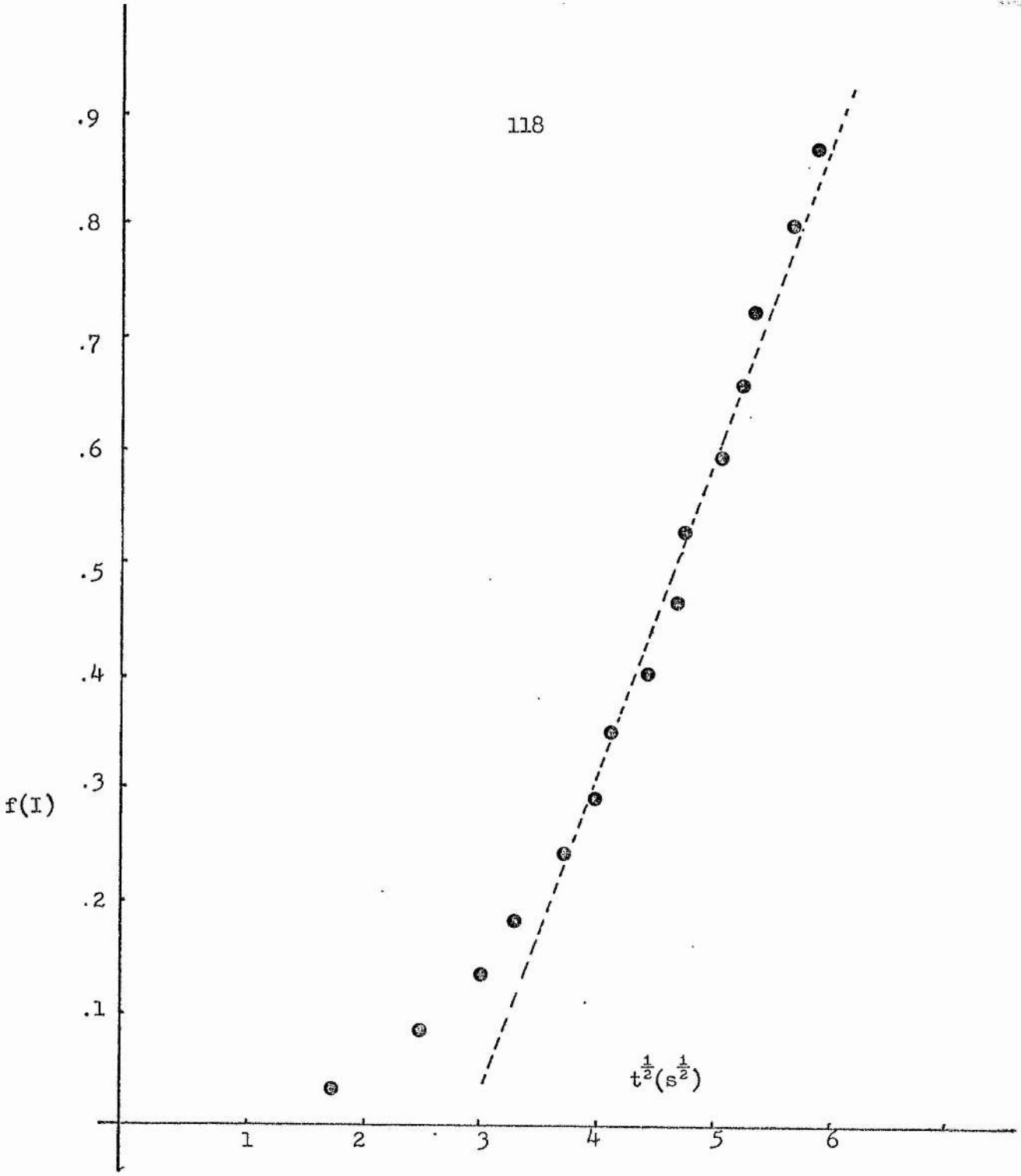


Figure 4.3

Diffusion plot for COR/PVA at 28°C.

4. (Ethylmethacrylate-Methylmethacrylate) 60%

Triphenylene in (EMA-MMA) 60% used as an additive to measure D for O_2 in this matrix over a range of temperatures, below and above room temperature. The decay of fluor. was recorded graphically. The results are summarised in Table 4.3 and shown in figure 4.4

Table 4.3

Diffusion of O_2 in (EMA-MMA) 60%

System	T(°C)	D ($cm^2\ s^{-1}$)
Tri/(EMA-MMA) 60%	0	9×10^{-10}
	29.7	4×10^{-9}
	57.6	8.2×10^{-9}

The diffusion coefficient over the above range of temperatures fitted to the general equation (Equ. 4.13) with ${}^{o}D = 1.1 \times 10^{-3}\ cm^2 s^{-1}$, and $E = 32.25\ kJ\ mole^{-1}$. That equation fitted the experimental data yielding an average error of $\mp$ 1.6% (fig. 4.5).

5. (St-MMA) 20% co-polymer

The method described in reference 130 was used to measure D of O_2 in (St-MMA) 20% copolymer and naphthalene was used as a suitable additive. The film, supported on a quartz disc, was placed in a thermostatted cell which could be rapidly flushed out with N_2 or O_2. The initial intensity, I_e^o (at t = o) was obtained by flushing out the cell with oxygen-free nitrogen until a constant intensity of emission, ${}^{o}I_e$, was obtained. The nitrogen stream was then replaced by a stream of dried O_2 and the fall-off in intensity measured as

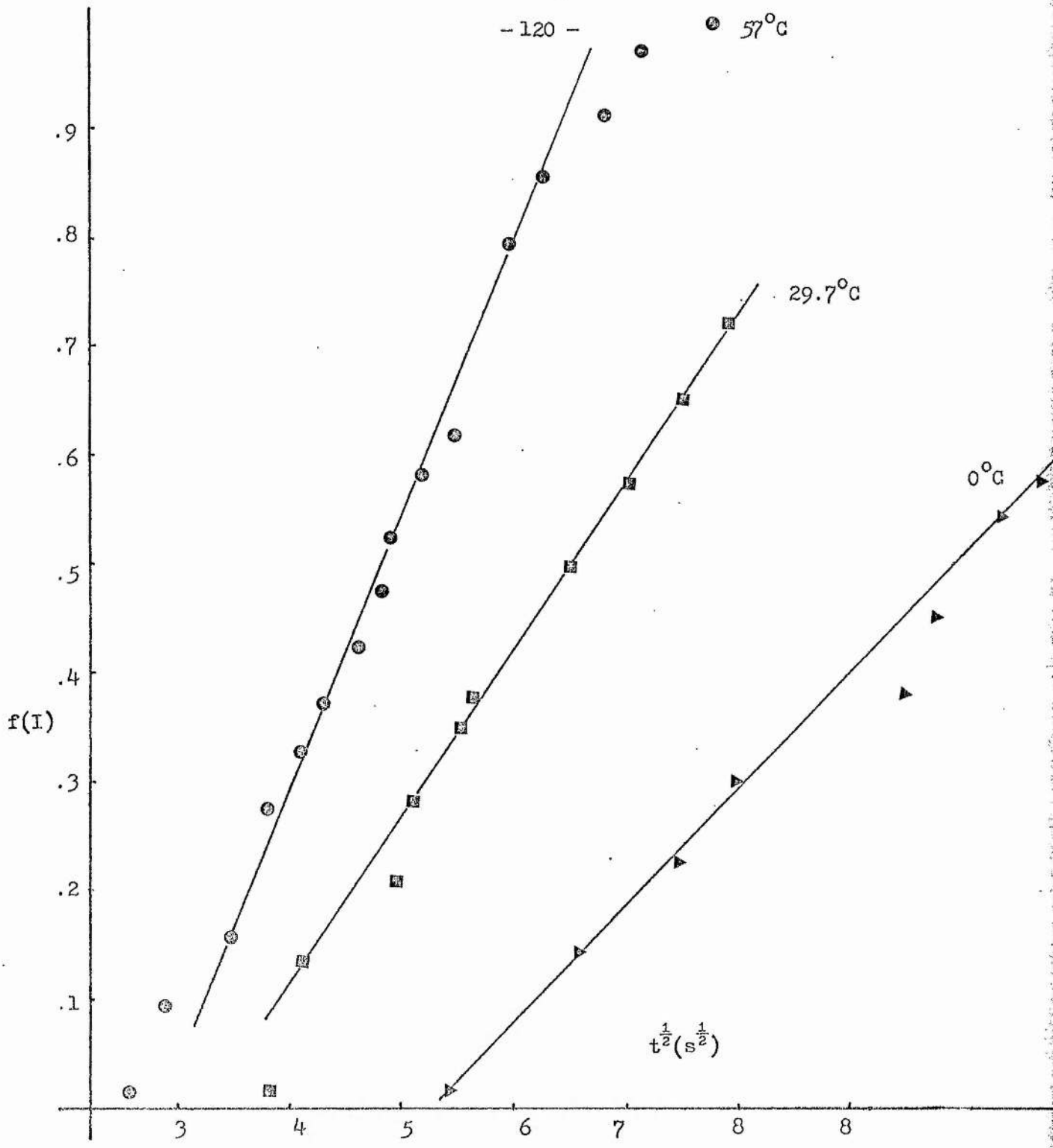


Figure 4.4

Diffusion for Tri/(EMA-MMA) 60% at different temperatures, 0°C, (▶); 29.7°C, (■); and 57°C; (●).

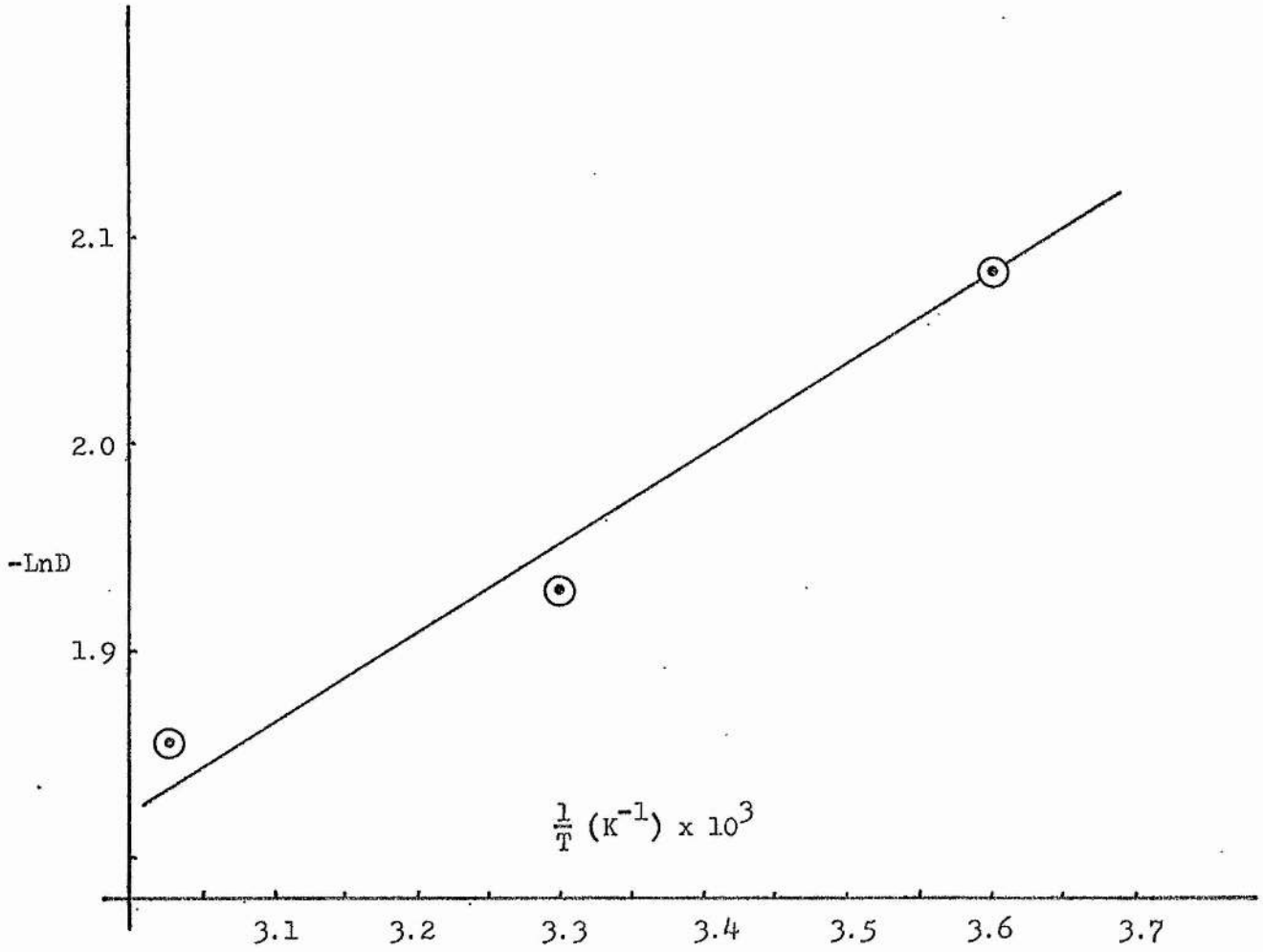


Figure 4.5

Temperature dependence of diffusion coefficients for T_{ri}/(EMA-MMA) 60%. Full lines are detained from linear regression analysis.

a function of time till a steady value, I_e^s, was given. Results of measurements carried out over a range of temperatures are shown in figure 4.6 and indicated in Table 4.4.

Table 4.4

Diffusion of oxygen in (St-MMA) 20% copolymer

System	T(°C)	D(cm^2 s^{-1})
N/(St-MMA) 20%	25	7.7×10^{-9}
	29.3	1.6×10^{-8}
	40.3	2.29×10^{-8}
	49.6	1.96×10^{-8}
	70	3.28×10^{-8}
	81.9	8.17×10^{-8}
	90	9.96×10^{-8}
	100	1.45×10^{-7}
	110.5	1.26×10^{-7}

°D was found to be 1.3×10^{-3} cm^2 s^{-1} and ΔE = 30.18 kJ $mole^{-1}$ within experimental error of ∓ 3.3%.

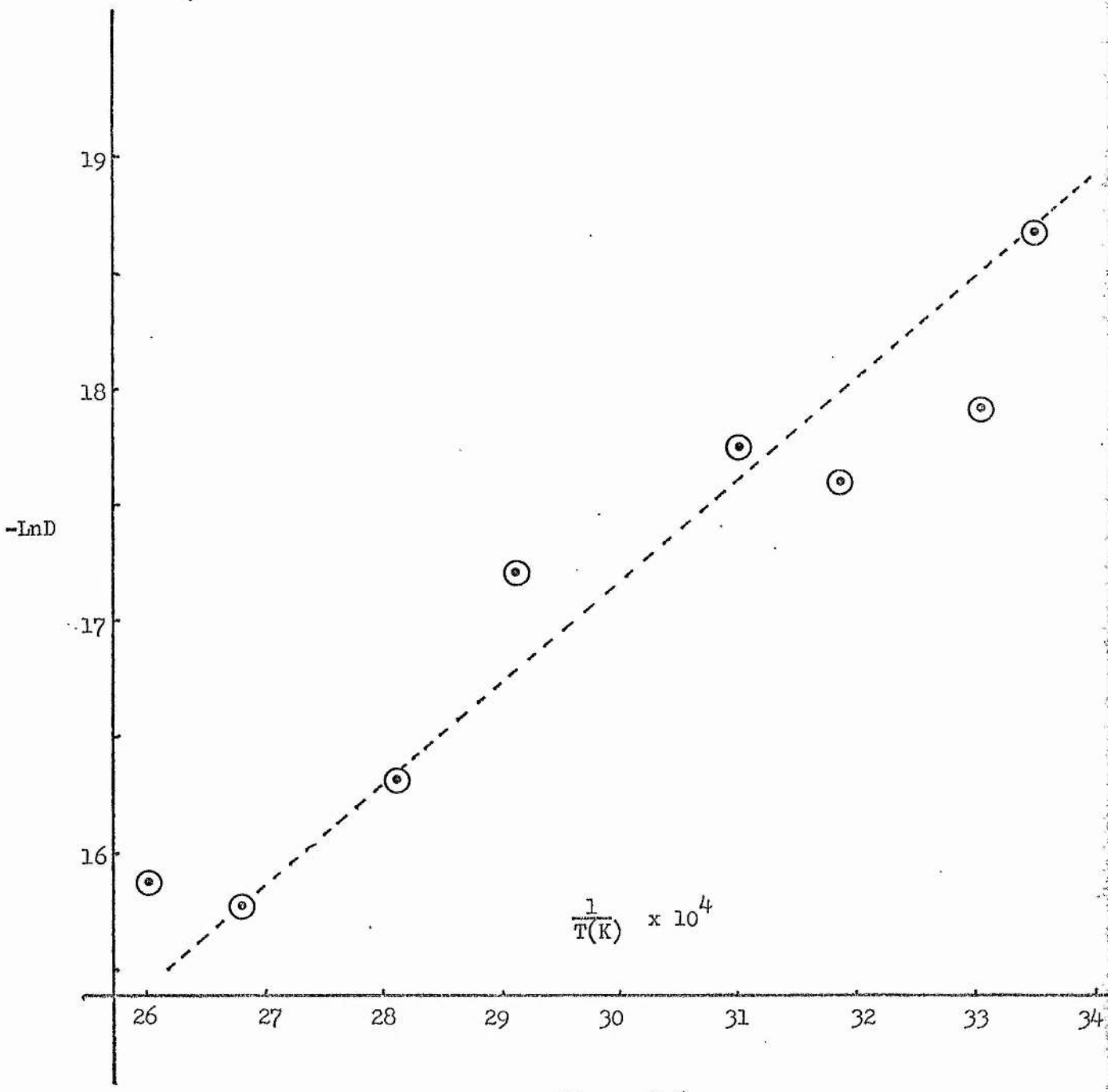


Figure 4.6

Temperature dependence of diffusion coefficient for N/(St-MMA) 20%. Full lines are obtained from linear regression analysis.

CHAPTER 5

Discussion

It is unexpected that coronene and triphenylene fluorescence intensity increases on admission of O_2. To give a reasonable explanation for this observation, it is convenient to consider the interaction between excited states of polymers and additives under different circumstances.

1. In vacuum

Our investigations in vacuum found the 'overshoot' behaviour of fluorescence for both coronene and triphenylene. In the latter case high intensity of irradiation was required. Coronene phosphorescence at R.T. in all the matrices investigated was exponential, while triphenylene phosphorescence was exponential in PMMA and almost exponential in PVA. However in Pst it was non-exponential.

To explain these observations, the following endothermic energy transfer step is postulated:

$$T_A + {}^{o}S_p \longrightarrow {}^{o}S_A + T_p \qquad 5.1$$

where A represents the additive and p the polymer. This proposal is related to the triplet energy levels shown in Table 5.1.

TABLE 5.1

Triplet energy levels of aromatics and polymers investigated in kJ mol^{-1}.

Compound	ΔE_{ST}	E_T	References
Coronene	46.6	228.8	38 (in PMMA)
Triphenylene	74.9	278.7	71
Phenanthrene	86.5	257.9	71
Naphthalene	130.6	253.7	71
PMMA	-	297.4	39
Pst	81.25	285.9	137
Oxygen	93.6	0	92-94

From this table we can see that the triplets of Pst and triphenylene are almost isoenergetic, thus energy transfer is likely and would be fast. The energy gap between the same additive and PMMA is about 20 kJ mol^{-1}, thus the process is endothermic and expected to be less likely and slow[140]. The exponential phosphorescence decay of triphenylene in PMMA and its non-exponential behaviour in Pst at R.T. support our explanation. It is quite clear that the triplet level of coronene is far moved from those of the matrices consequently triplet energy transfer is highly endothermic, and as a result its phosphorescence decay was found to be exponential at room temperature. In order to give a reasonable explanation for the non-exponential behaviour of triphenylene in Pst matrix, involvement of another step

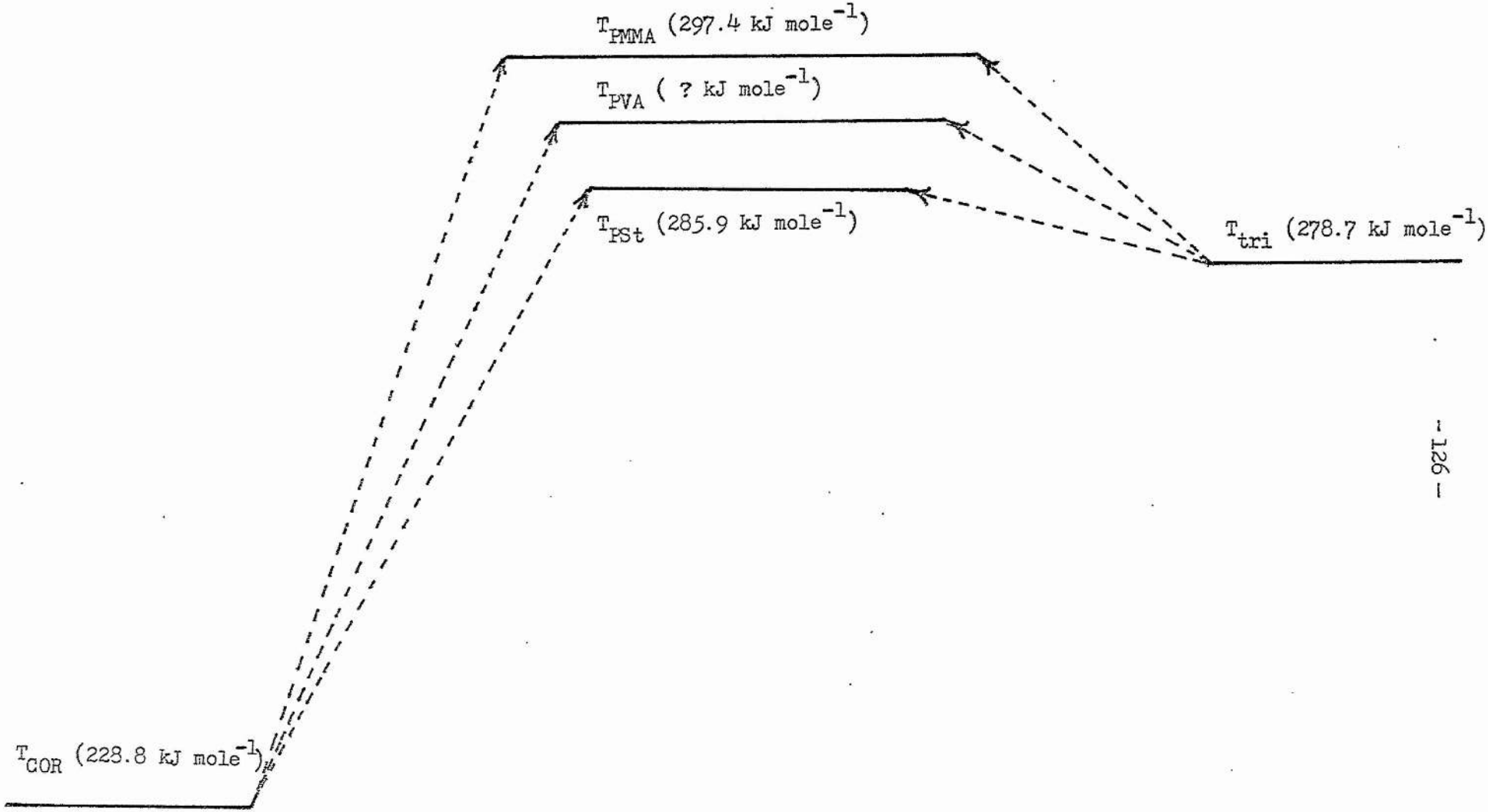


Figure 5.1

Diagram of energy transfer from excited triplet state of additives to the triplet state of polymers.

(energy migration) can be considered:

$$T_p + {}^oS_p \longrightarrow {}^oS_p + T_p \qquad 5.2$$

along with

$$T_p + {}^oS_{tri} \longrightarrow {}^oS_p + T_{tri} \qquad 5.3$$

and the total effect is to produce a mobile triplet exciton. A further possibility now exists:

$$T + T \xrightarrow{k_{TT}} {}^oS + {}^oS\,({}^1S) \qquad 5.4$$

The effect of such a step on the kinetics of phosphorescence decay is to introduce a contribution from the second order reaction which disturbs the exponential decay. Equation (5.5) gives the correct expression for this type of decay:

$$T = \left\{ \left(\frac{1}{[T]_o} + \frac{k_{TT}}{k_1} \right) \exp k_1 t - \frac{k_{TT}}{k_1} \right\}^{-1} \qquad 5.5$$

k_1 represents the sum of the unimolecular decay processes. Since we are unable to follow T directly it is not possible to test this equation from the experimental data.

In summary, as triplet transfer to polymer becomes more likely, either as a result of a small energy gap or by increasing temperature, and step (5.5) becomes more significant so non-exponential decay is observed. Although the depolarisation measurements are somewhat inconclusive in that much experimental scatter appears in the observations, previous workers have also observed that the triplet emission

remains largely polarised[138]. This would tend to preclude additive mobility which is necessary for:

$$T_{tri} + T_{tri} \longrightarrow {}^{o}S_{tri} + {}^{1}S_{tri}$$

However on the basis of a mobile polymer triplet exciton it is possible to have

$$T_{p} + T_{tri} \longrightarrow {}^{o}S_{p} + {}^{1}S_{tri}$$

without loss of polarisation by the triplet triphenylene.

Turning to the "overshoot" behaviour in vacuum, the following explanation is suggested:

$$^{1}S_{A} + T_{p} \longrightarrow {}^{o}S_{A} + T_{p} \qquad 5.6$$

5.6 represents a quenching step brought about by the mobile, paramagnetic triplet exciton. Although T_p will be low in concentration it could have an enhanced activity due to rapid diffusion by a hopping mechanism.

The following scheme describes the photophysical processes involved:

$$^{o}S_{A} + h\nu \xrightarrow{k_1} {}^{1}S_{A}$$

$$^{1}S_{A} \xrightarrow{k_2} {}^{o}S_{A} + \text{heat}$$

$$^{1}S_{A} \xrightarrow{k_3} {}^{o}S_{A} + h\tilde{\nu} \qquad \text{(fluorescence)}$$

$$^1S_A \xrightarrow{k_4} T_A$$

$$^1S_A + T \xrightarrow{k_5} {}^0S_A + T \qquad \text{(paramagnetic quenching)}$$

$$T_A \xrightarrow{k_6} {}^0S_A + \text{heat}$$

$$T_A \xrightarrow{k_7} {}^0S_A + h\nu'' \qquad \text{(phosphorescence)}$$

$$T_A + {}^0S_p \xrightarrow{k_8} {}^0S_A + T_p \qquad \text{(energy transfer)}$$

$$T_p + {}^0S_p \xrightarrow{k_9} {}^0S_p + T_p \qquad \text{(energy migration)}$$

$$T_p + {}^0S_A \xrightarrow{k_{10}} {}^0S_p + T_A \qquad \text{(reverse energy migration)}$$

$$T_p + T_A \xrightarrow{k_{11}} {}^1S_A + {}^0S_p$$

This scheme does not analysis readily, but qualitatively it illustrates the decrease of intensity of fluorescence as the concentration of T species rises, as observed.

2. Temperature effect

Endothermic transfer increases with increasing temperature. Triphenylene phos. decay is exponential in PMMA and almost exponential in PVA (fig. 3.12). The kink in $\ln \tau$ vs. $\frac{1}{T(K)}$ corresponds to the temperature at which T + T mechanism becomes important (fig. 3.13). The activation energy for the exponential behaviour part of tri. in PMMA corresponds to the energy gap between their triplet levels. Our

value in PMMA is not accurate because of back donation[140]. We found this activation energy to be 10.4 kJ mol^{-1} in PMMA and 7.9 kJ mol^{-1} in PVA, a point which indicates that the triplet level of PVA lies below that of PMMA and above polystyrene's level (see fig. 5.1). Once again the triphenylene phosphorescence decay in PVA supports this conclusion.

3. Oxygen effect

In fact, it is not so easy to give a sufficient reason for why molecular oxygen acted as an enhancer of fluorescence of coronene and triphenylene in polymer matrices. The following scheme which describes the important reactions involved in vacuum and under O_2 is postulated:

Reaction	Rate
$^0S \xrightarrow{h\nu} {}^1S$	I_a
$^1S \longrightarrow {}^0S$ + heat	$k_2 [{}^1S]$
$^1S \longrightarrow {}^0S + h\nu'$	$k_3 [{}^1S]$
$^1S \longrightarrow T_A$	$k_4 [{}^1S]$
$^1S + T_p \longrightarrow {}^0S + T_p$	$k_5 [{}^1S][T]$
$^1S + {}^3O_2 \longrightarrow {}^0S + {}^3O_2$	$k_6 [{}^1S][{}^3O_2]$

$$T_A \longrightarrow {}^{o}S + \text{heat} \qquad k_7 [T_A]$$

$$T_A \longrightarrow {}^{o}S + h\nu'' \qquad k_8 [T_A]$$

$$T_p + {}^{o}S_p \longrightarrow {}^{o}S_A + T_p \qquad k_9 [T_p][{}^{o}S_p]$$

$$T + {}^{3}O_2 \longrightarrow {}^{o}S + {}^{1}O_2 \qquad k_{10} [T][{}^{3}O_2]$$

$${}^{1}O_2 \longrightarrow {}^{3}O_2 \qquad k_{11} [{}^{1}O_2]$$

$$T_A + {}^{1}O_2 \longrightarrow {}^{1}S + {}^{3}O_2 \qquad k_{12} [T_A][{}^{1}O_2]$$

At steady state of $[T]$ and in vacuum:

$$\frac{d[T]}{dt} = k_4 [{}^{1}S] - k_7 [T] - k_8 [T] \qquad 5.6$$

when the light is cut-off,

$$[{}^{1}S] = 0$$

and

$$-\frac{d[T]}{dt} = (k_7 + k_8)[T] \qquad 5.7$$

Equation (5.7) is first order in form, and our experimental result, the exponential behaviour in vacuum, supports this mechanism.

When O_2 is present, and for the condition of a steady concentration state of $^1O_2$:

$$k_{10}\,[T_A]\,[^3O_2] = k_{11}\,[^1O_2] + k_{12}\,[T_A]\,[^1O_2] \qquad 5.8$$

$$[^1O_2] = \frac{k_{10}\,[T_A]\,[^3O_2]}{k_{11} + k_{12}\,[T_A]}$$

$$= \frac{k_{10}}{k_{11}}\,[T_A]\,[^3O_2] + \frac{k_{10}}{k_{12}}\,[^3O_2] \qquad 5.9$$

At the steady state of $[T]$ under O_2

$$\frac{d[T]}{dt} = k_4\,[^1S] - k_7\,[T] - k_8\,[T]$$

$$- k_9\,[T]\,[^0S_p] - k_{10}\,[T]\,[^3O_2]$$

$$- k_{12}\,[T]\,[^1O_2]$$

when the light is cut-off $[^1S] = 0$

$$-\frac{d[T]}{dt} = [T]\,(k_7 + k_8 + k_9\,[^0S_p] + k_{10}\,[^3O_2])$$

$$+ k_{12}\,[T]\,[^1O_2] \qquad 5.10$$

substitution of equation (5.9) in equation (5.10) results in:

$$- \frac{d[T]}{dt} = [T](k_7 + k_8 + k_9 [{}^0S_p] + k_{10} [{}^3O_2]) + k_{12} [T] \left(\frac{k_{10}}{k_{11}} [T] [{}^3O_2] + \frac{k_{10}}{k_{12}} [{}^3O_2] \right)$$

$$= [T] (k_7 + k_8 + k_9 [{}^0S_p]) + k_{10} [T] [{}^3O_2] + \frac{k_{10} k_{12}}{k_{11}} [{}^3O_2] [T]^2 + k_{10} [T] [{}^3O_2] \qquad 5.11$$

For simplicity it can be written in the following form

$$- \frac{d[T]}{dt} = A [T] + B [T]^2 \qquad 5.12$$

where A and B are constants with

$$A = k_7 + k_8 + k_9 [{}^0S_p] + 2k_{10} [{}^3O_2] .$$

and

$$B = \frac{k_{10} k_{12}}{k_{11}} [{}^3O_2]$$

Equation 5.12 is mixed first and second order and explain the non-exponential behaviour of triphenylene and coronene under O_2 (figure 3.10 and 3. 30), (See equation 5.5). Furthermore adding step 10 to step 12 gives the non-exponential behaviour (T + T) as follows:

$$T + {}^3O_2 \longrightarrow {}^oS + {}^1O_2$$

$$T + {}^1O_2 \longrightarrow {}^1S + {}^3O_2$$

$$T + T \longrightarrow {}^1S + {}^oS$$

Non-exponential decay of 1,2,5,6-dibenzanthracene phosphorescence dissolved in PVA in low pressure of O_2 at R.T. has been reported[145]. No mechanism was proposed.

When oxygen interacts with a polymer film containing excited additives, the overall mechanism is disturbed mainly through steps (10) and (12)

$$^1S + T \xrightarrow{k_{10}} {}^oS + T$$

$$T + {}^1O_2 \xrightarrow{k_{12}} {}^1S + {}^3O_2$$

Step (10) is governed by the mobility of T_p and (12) by ΔE_{ST}, the energy gap between T and ^1S. The vacuum effect suggest T_p is mobile and from table 5.1 it can be seen that ΔE_{ST} for coronene and triphenylene is less than $\Delta E_{{}^1O_2 \rightarrow {}^3O_2}$. Admission of O_2 to an evacuated system will quench the triplet and release ^1S by (10) and also produce ^1S via (12). In fact, it is not easy to find which of the two mechanisms is more efficient. When cyasorb 1084, a singlet oxygen quencher[116,118], was cast with triphenylene in PMMA, it reduced the fluorescence enhancement by 50%. This

observation is good evidence for the participation of $^1O_2$ as written in step (12). A similar experiment with coronene (also using DABCO) showed no marked change in fluorescence intensity on admitting O_2 (see page 77). However when NO, a paramagnetic species, was added to a PMMA film containing coronene, the fluorescence increased (see page 83). This can be accounted for by step (10), that is $[T]$ decreases due to efficient quenching by NO (fig. 3.31).

The relative importance of (10) and (12) is governed by the nature of the additive and the matrix. For triphenylene in PMMA (12) is more important, whereas (10) predominates for coronene in all polymers.

The literature contains similar findings in polymer matrices[141-143]. Jones and Nesbitt[143] attribute the oxygen enhanced fluorescence to a trivial mechanism. Since the organic molecules which exhibit fluorescence enhancement have long triplet life times (of the order of a second or more), with exciting radiation of reasonable intensity, an evacuated sample could achieve a relatively high steady state triplet concentration, reducing the number of ground state additive molecules, available for direct excitation to the singlet manifold. When the sample is exposed to oxygen, the triplet life time is drastically reduced by the quenching process, covering an increase in the ground state population of the guest molecule and hence in the amount of observed fluorescence. This mechanism was rejected because they estimate that its effect would be too small to account for the magnitude of the fluorescence enhancement observed. Kenner and Khan[144] using a completely different technique based on observation of phosphorescence emission proposed a singlet oxygen "feed-back" mechanism for the oxygen stimulated fluorescence of chrysene in

polystyrene fluffs.

However, in all cases the enhanced fluorescence is related to the presence of the triplet state of additives. When the triplet was completely removed by low pressure of O_2, we did not observe this strange enhanced fluorescence in coronene (see page 83) and in triphenylene (fig. 3.9). As listed in Table 3.13, k_qK in Pst and in PEMA are higher than that in PMMA for the same additive. This can be explained by the effect of K, the distribution constant, which is likely to be larger in these polymers than in PMMA.

4. Low Temperature Quenching by Polymer Units

Previous workers have investigated the phosphorescence behaviour of triphenylene at 77K in polystyrene[137] and in poly(methylmethacrylate)[39]. Similar differences in $\tau_{Phos.}$ were observed although Offen[137] found that pressure cycling affected the apparent life time. During preliminary experiments in the present work it was observed that preparation of samples by thermal polymerisation of styrene always resulted in specimens containing unpolymerised monomer. The presence of monomer would complicate subsequent observation of emission spectra. The use of purified samples of polymers in casting thin films containing the additives is considered to be much more satisfactory for preparing samples.

The decrease in $\tau_{Phos.}$ must be caused by quenching of the triplet additives by the polymer matrix, the styrene unit being more efficient than the methylmethacrylate. The following mechanism for depletion of the aromatic triplet population is proposed:

$$T_A \xrightarrow{k_1} {}^{o}S_A$$

$$T_A \xrightarrow{k_2} {}^{o}S_A + h\nu$$

$$T_A + {}^{o}S_{P_{M,S}} \xrightarrow{k_q} {}^{o}S_A + T_{P_{M,S}} \text{ or } S^{o}_{P_{M,S}} \qquad 5.13$$

in which A represents a coronene or triphenylene molecule, P_M a methylmethacrylate unit, and P_S a styrene unit in the polymer. Following cessation of excitation the decay of triplet species can be described thus:

$$-\frac{d[T_A]}{dt} = (k_1 + k_2)[T_A] + k_{qm}[P_M][T_A] + k_{qs}[P_s][T_A]$$

From which it can be deduced that:

$$\frac{1}{\tau_A} = \frac{1}{{}^{o}\tau_A} + k_{qm}[P_m] + k_{qs}[P_s] \qquad 5.14$$

It is convenient to use mole fraction (χ) in equation (5.14) rather than molarities of copolymer units. Thus

$$\chi_m = \frac{[P_m]}{[P_m] + [P_s]}$$

and

$$\chi_s = \frac{[P_s]}{[P_m] + [P_s]}$$

and following substitution in equation (5.14) that equation

rearranges to:

$$\frac{1}{\tau_A} = \frac{1}{{}^{o}\tau_A} + k_{qm}([P_m] + [P_s]) + \chi_s(k_{qs} - k_{qm})([P_m] + [P_s]) \qquad 5.15$$

Equation (5.15) confirms the linear relationship between $\frac{1}{\tau_A}$ and χ_s, shown in figures 5.2 and 5.3 , and facilitates calculation of k_{qm} and k_{qs} making use of $({}^{o}\tau_A)^{-1}$ available from the literature. The values obtained are shown in Table 5.2

TABLE 5.2

Quenching constants from MMA/St copolymers at 77K

Additive	k_{qs} (l mole^{-1} s^{-1})	k_{qm} (l mole^{-1} s^{-1})
Triphenylene	2.8×10^{-3}	7.8×10^{-4}
Coronene	2.9×10^{-3}	0 *

* value for coronene derived using ${}^{o}\tau_A$ from ref. (145).

$k_{q_s} > k_{q_m}$ for both polycyclic aromatics and we propose that energy transfer may be responsible for the quenching process.

Referring to table 5.1 it can be seen that the endothermicity of

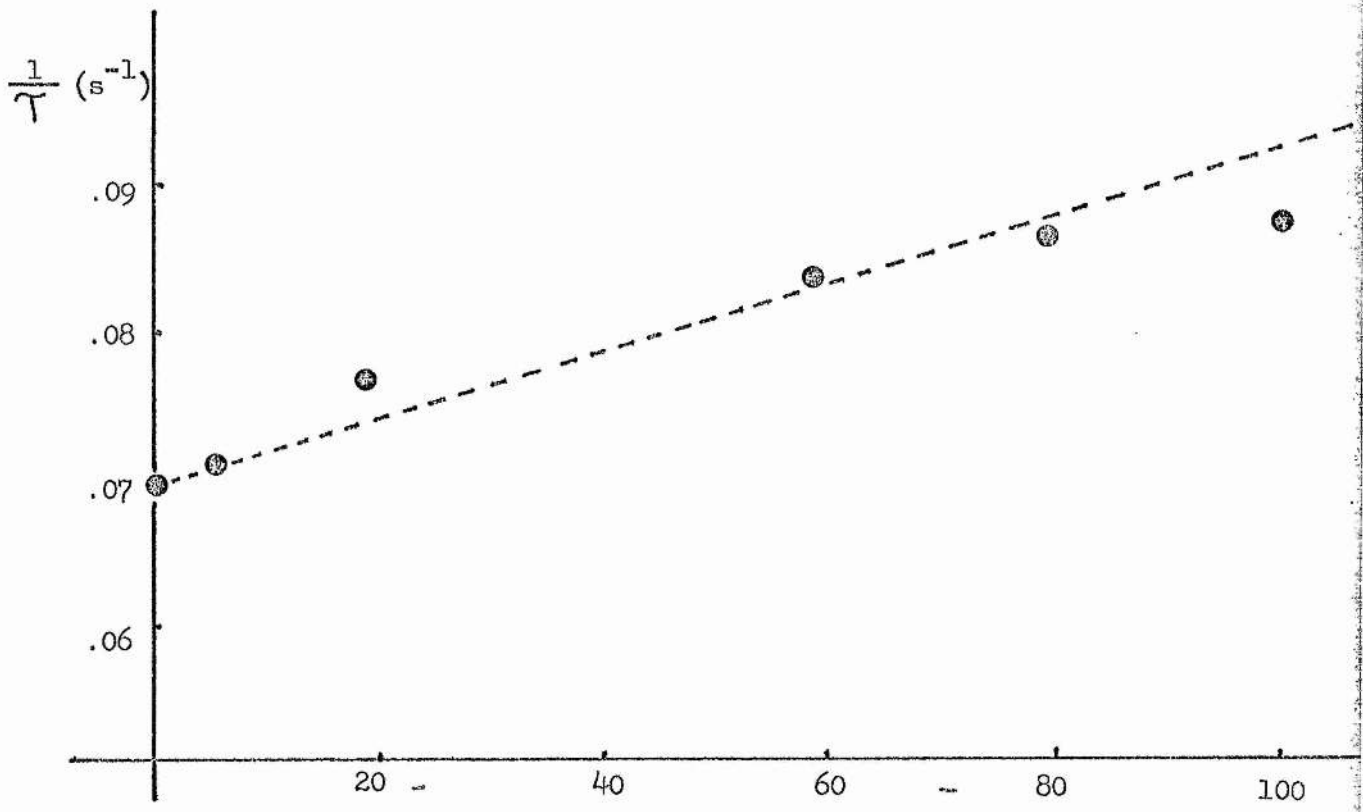


Figure 5.2

$\frac{1}{\tau}$ for triphenylene phosphorescence vs. mole fraction of St. unit in St.MMA copolymer at 77K.

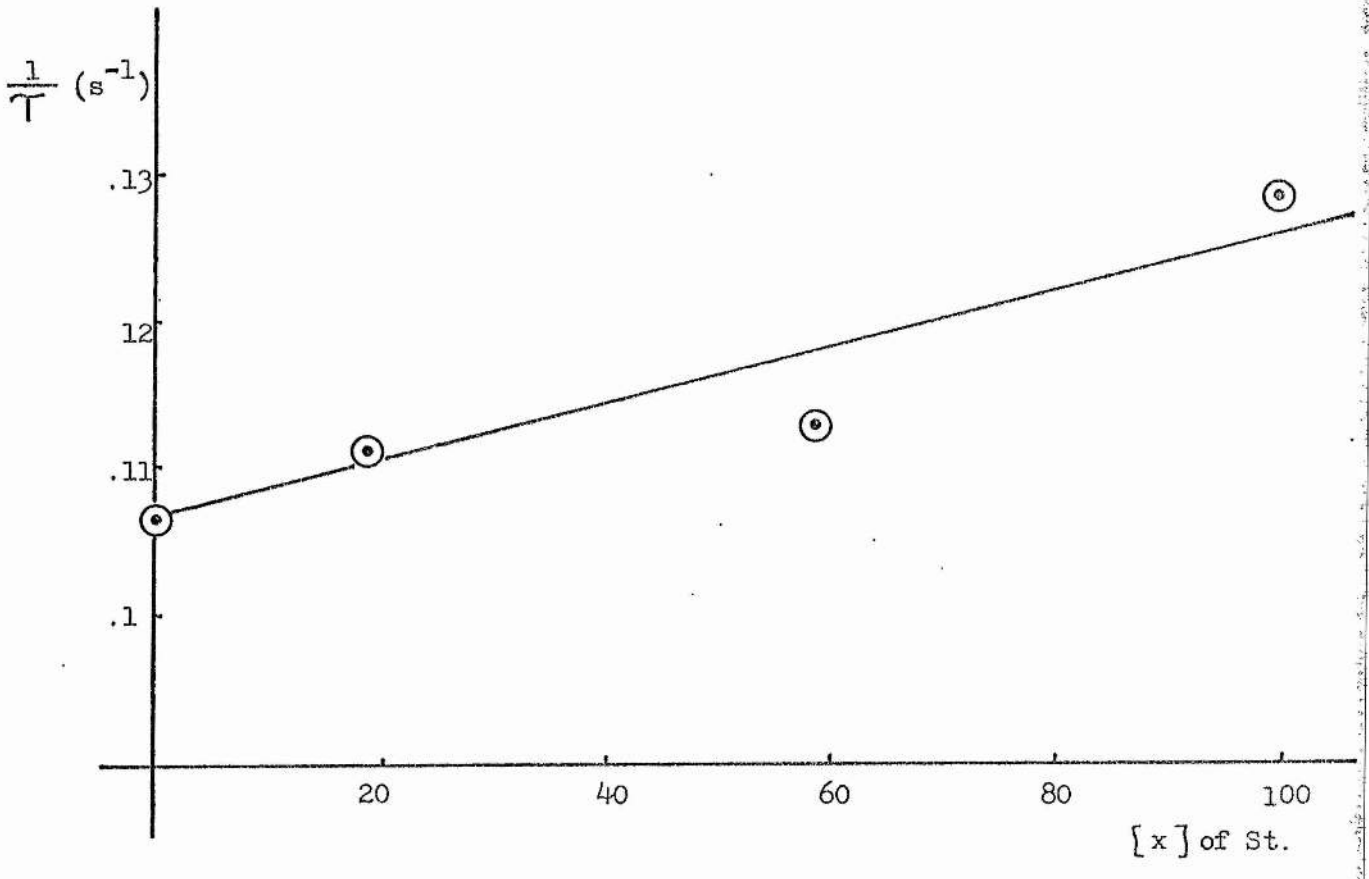


Figure 5.3

$\frac{1}{\tau}$ for coronene phosphorescence vs. mole fraction of St. unit in St.MMA copolymers at 77K.

the triphenylene/styrene transfer is much less than for coronene/ styrene, however the quenching constants measured at 77K indicate similar values for these constants. It would require a very large difference in the pre-exponential factor to account for this apparent contradiction. It is also important to note that all the decays measured at 77K were exponential thus ruling out T + T reactions. Therefore the quenching reaction may not be one of energy transfer but some process of static quenching via complex formation of the triplet and polymer matrix:

$$T_A + {}^{o}S_{p_{m,s}} \longrightarrow (T_A - {}^{o}S_{p_{m,s}}) \longrightarrow {}^{o}S_A + {}^{o}S_{p_{m,s}}$$

Formation of such a complex would allow this spin-forbidden step to occur.

5. Quenching by "DABCO" in toluene

Table 3.14 and figure 3.42 show that DABCO is a good quencher for singlet excited state of aromatic molecules in solution. Anthracene, perylene and naphthalene showed a good S/V plots, and DABCO quenches at diffusion controlled rate. In nitrogen phenanthrene appears to be quenched 10 times faster than in air. Coronene does not seem to follow S/V type quenching, the k_q value is much lower than the others and it increased when O_2 is present (assuming τ is correct). The non linear plot observed for coronene in PMMA was also found in toluene solutions.

6. Diffusion

Our results are in agreement with published work for diffusion of O_2 in PMMA, Pst and PVA. No literature values in St.MMA copolymers are available or at low temperature to compare with these recorded in Chapter 4. The diffusion constant increased with decreasing O_2 pressure, a point which is considered as casting some doubt on the validity of Fick's law in this case.

Conclusion

The results of this thesis provide good evidence for energy transfer to the polymeric matrix, confirming the conclusions proposed by McGlynn. In addition the data obtained suggest triplet exciton mobility.

Moreover, these results substantiate the singlet O_2 mechanism given by Kenner and Khan, but also add an extra step. Finally once the enhancement effect was understood more clearly it then allowed use of the fluorescence technique to evaluate the diffusion constant of oxygen under a variety of conditions.

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